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THE FOUNDATIONS OF CHEMISTRY.[1]

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1. In an essay published forty years since, in September, 1848, the present writer advanced as the "basis of a true natural system of chemical classification," certain views as to elemental and polymeric types which have since played an important part in the science of chemistry. Assuming as the primal or fundamental type, hydrogen, H_2 (of which both water and ammonia were regarded as derivatives), and following the lead of Auguste Laurent, who had already, in 1846, represented alcohol and ether as derivatives of water, H_2O, in which one and two portions of hydrogen respectively are replaced by C_2H_3,[2] the hydrocarbons methane and ethane were considered as derivatives of H_2, in which one portion of hydrogen is replaced by CH_3 and C_2H_5. The relation between these hydrocarbons and hydrogen, and between the corresponding alcohols and water, was then declared to be one of homology, and these views were subsequently maintained and enforced on many occasions.[3]

[1] Read before the National Academy of Sciences, April 17, 1888.

[2] Being H_3O_3 and C_4H_6 in the notation then in use, in which H = 1, C = 6 and O = 8.

[3] On Some Anomalies in the Atomic Volume of Sulphur, etc., with Remarks on Chemical Classification, American Journal of Science (Sept., 1848) **6**, 170-178; also, On Some Principles to be Considered in Chemical Classification, read before the American Association for the Advancement of Science, Philadelphia (1848). Ibid. 1849, **7**, 399; **8**, 89; (also **5**, 265; **9**, 65; **13**, 206); and further, The Theoretical Relations of Water and Hydrogen (1854), ibid. **17**, 194, and Chemical Gazette, 1854, p. 181; also, The Theory of Types in Chemistry (1861), Amer. Jour. Science **31**, 256, and Hunt's Chemical and Geological Essays (pp. 464-469).

2. In the same essay the writer insisted on the existence of condensed or polymeric types, the pentachlorides being "referrible to a triple molecule, represented by H, while the corresponding trichlorides form a double molecule." The triple molecule was further said to be represented by the vapor of sulphur, then known only in its hexad form, S_6, the anomalous density of which, as compared with that of oxygen, was explained as the result of polymerism or condensation, while a similar condensation was suggested as probable in the case of ozone. The derivation of monobasic acids from the type of water, H_2O, and the possibility of anhydrides of these, and notably of the nitric anhydride (soon afterwards discovered by H. Deville), was also maintained in this essay; while bibasic and tribasic acids were regarded as derived from condensed types corresponding to two and three molecules of water. Hydrogen, H_2, was then both the prototype and the homologue of the hydrocarbons and the chlorides, and water, H_2O, of alcohols, ethers, oxacids and anhydrides.

3. There were thus enunciated in this essay, in 1848, two distinct and important conceptions: (1) Hydrogen, H_2, is the primal chemical type, of which water and ammonia are derivatives, and to which both mineral and so-called organic or hydrocarbonaceous types may be referred. (2) Besides this dual or normal type, represented by H_2, there are also condensed or polymeric types, represented respectively by H_4 and by H_6, S_3, etc., the condensation being made evident by the increased density of the polymeric vapors. How the first of these conceptions, that of the typical relations of water and hydrogen, after having been maintained for some years, was at length adopted by Gerhardt, Brodie, and Williamson, in 1851–1852, is to-day a matter of history, and is set forth in the two papers of 1854 and 1861, already cited, in the latter of which will be found quoted a full recognition by Wolcott Gibbs of the writer's claims to priority. The second and not less important conception—that condensed or polymeric types, as represented by the higher metallic chlorides and the dense vapor of sulphur, remained, however, apparently unnoticed by chemists until after its restatement in 1854, when it was adopted by Ad. Wurtz.

4. Meanwhile the writer, in the essay already noticed, "On Some Principles to be Considered in Chemical Classification" (read in 1848 and published in 1849), had still further considered this con-

ception of polymerism with increase of specific gravity, which was then extended from vapors to solid species, and was illustrated by the allotropic modifications of carbon and of phosphorus. In 1853 an attempt was, moreover, made to show that the change from a gaseous to a liquid or solid species is itself subjected to the same general law of polymerism; while in 1867 it was maintained that vapors, and the liquid and solid products of their condensation, as in the case of steam, water, and ice, are to be regarded as distinct species, the latter two being polymeric or allotropic forms of water vapor; in a word, that all changes of state or condition in bodies are essentially chemical in their nature.[1] Similar views as to the chemical relations of gaseous, liquid and solid species were, thirty years later, in 1883, set forth by Prof. W. Spring, of Liège,[2] to whom my earlier discussions of the subject were unknown.

Continuing the line of inquiry thus begun, and followed at intervals during forty years, it is now proposed to consider briefly the relations of gaseous, liquid and solid species to temperature and pressure, together with the phenomena of allotropism, of specific gravity, of hardness, and of chemical indifference; all of which, as we have elsewhere maintained, are intimately related to and dependent upon the principle of condensation then enunciated.

5. All chemical change, of which this polymerism or condensation is but one manifestation, is subordinated to simple relations of weight and volume, which are most evident in the case of volatile and gaseous species. Well-defined gases, such as hydrogen, nitrogen, oxygen, carbon monoxide and methane, undergo, through a wide range of temperature, a constant regular change of volume, amounting for each degree centigrade to $\frac{1}{273}$ of their volume at 0°. Their coefficient of expansion not being sensibly affected by considerable variations of pressure (which, according to Boyle's or Marriotte's law, the temperature being constant, causes the volume to vary inversely as the pressure), it follows that if we know the weight of a volume of such a gas at any given temperature and pressure, it is easy to calculate what its weight should be at any other temperature and any other pressure; as for example at 0° and

[1] Theory of Chemical Changes and Equivalent Volumes, 1853; American Journal of Science **15**, 226; L. E. and D. Philos. Magazine (4), **5**, 26; and in German translation, Chem. Centrbl. 1853, 849; also, The Objects and Methods of Mineralogy (1867), American Journal of Science **13**, 203. These two papers are reprinted in the author's Chemical Essays, 426-437 and 453-458. See also, A New Basis for Chemistry, etc., §§20-22.

[2] Sur l'élasticité parfaite des corps solides chimiquement definis. Bull. de l'Acad. Roy. de Belgique (2), **6**, No. 11.

760 mm., which are assumed as the standards in studying gases and vapors. These regular and constant variations in the weight and volume of a species under changes of temperature and pressure characterise the perfect or ideal gaseous state of matter. This is, however, known to us only within certain limits, since recent experiments have shown that the gases mentioned above are by the combined action of cold and pressure reduced to the state of liquids which, although still more or less compressible, are not subject to Boyle's law, and, moreover, often present great and rapidly increasing coefficients of expansion by heat; a point especially noticeable in liquids as they approach the critical point beyond which they pass, under great pressure, into dense vapors.

6. The ideal liquid, like the ideal gas, has a regular rate of thermic expansion, the coefficient of which, however, varies for the different species, and is apparently (like its compressibility) closely connected with the degree of condensation; that is to say with the interval by which it is removed from the normal gaseous species with which it is connected through dense vapors of higher integral weight. Water and mercury are, within considerable ranges of temperature, nearly ideal liquids. The ideal solid is, like the ideal liquid, permanent through considerable ranges of temperature, within which it has a regular coefficient of expansion of heat. It is sometimes more and sometimes less condensed than the corresponding liquid species; thus ice is considerably lighter than water, and solid bismuth is lighter than the fused metal, while in the greater number of cases the solid is heavier than the corresponding liquid species. For such liquids as become denser in solidification, it is well known that pressure augments their temperature of fusion. Amagat, in accordance with this principle, has reversed the well known experiment of liquefying ice by pressure, and has effected the solidification of carbon dichloride (hitherto known only in a liquid form) by a pressure of 900 atmospheres at 10°; while benzene, which under standard pressure crystallises only at 0°, is solidified at 22° under 700 atmospheres. There is probably, however, according to Amagat, "a temperature above which solidification cannot be effected by any pressure, that is to say, a critical point of solidification, as there is apparently a temperature below which the body remains solid under the feeblest pressure."[1]

On the other hand, it appears from many experiments that, in

[1] Comptes Rendus de l'Acad. des Sciences, July 18, 1887.

the language of W. Allen Miller, "there exists for every liquid a temperature at which no amount of pressure is sufficient to retain it in liquid form."[1] In other words, all such liquids and solid species, if stable—that is, not thereby undergoing heterogeneous dissociation—when heated under sufficient pressure to a temperature which for each is called its critical point, pass, with a comparatively small augmentation of volume, into the condition of very dense vapor or gas. The distinction between liquid and gas just above the critical point is, according to Andrews, impossible, and, in the language of Ramsay and Young, "would also disappear below the critical point, were it possible to follow the continuous change from liquid to gas."[2] In fact, the passage from the perfect or ideal gas proceeds through successively denser unstable polymeric gaseous or vaporous species, often more or less intermingled with one another, and perhaps also through unstable liquid species, into the ideal liquid or the ideal solid species.

7. We assume for the unit of volume in chemistry 1000 cubic centimeters or one liter, and for the unit of weight that of this volume of hydrogen at 0° and 760 mm., which equals very nearly 0.0896 gram, or, according to the determination of Regnault in the latitude of Paris, 0.089578 gram. In hydrogen, which through a wide range of temperature and pressure retains the properties of a perfect or ideal gas, we have a standard of weight upon which is built the stochiometry of modern chemistry. The weight of this volume of hydrogen at the temperature and pressure named being taken as unity (H = 1), that of a like volume of oxygen gas under the same conditions is approximately 16, or, more nearly, 15.96; that of nitrogen being 14, and that of chlorine 35.5. If now we bring together under these conditions of temperature and pressure two liters of hydrogen and one of oxygen gas, no change takes place until by the intervention of flame or the electric spark, or more slowly by the action of spongy platinum, their union is effected, with dissipation of radiant energy. The product of the integration of the two gases may exist at 0° either as solid ice or as liquid water. This latter at 100°, overcoming the atmospheric pressure of 760 mm., passes into water vapor, which at higher temperatures is subject to the common law governing the thermic expansion of gases, but at length reaches a point at which at standard pressure it undergoes heterogeneous disintegration, being resolved into its

[1] Miller. Chemical Physics, 3d edition. [2] L. E. & D. Philos. Magazine (5), **13**, 548.

constituent gaseous elements. The weight of a liter of water vapor is the sum of the weights of a liter of hydrogen and half a liter of oxygen, the volume of the latter, as well as the specific characters of both, having in the act of integration been lost in that of a new species, so that the weight of a liter of hydrogen at 0° and 760 mm. being unity = 1.00, that of a liter of water vapor reduced by calculation to the same standard temperature and pressure = 8.98. But as the combining weight for water vapor, or in other words its integral weight, is found to be twice that number, or 17.96, its volume is represented by two liters. It is thus, in the language of A. W. Hofmann, dilitral. When, in the older notation, the volume of eight parts of oxygen was assumed as the unit, O = 8, water vapor, then written H_2O_2, was said to consist of four volumes of hydrogen and two of oxygen condensed into four volumes of vapor.

8. The condensation which appears in the union of hydrogen and oxygen gases to form water vapor has been defined as interpenetration, but is more properly an identification of volume, or, to use Herbert Spencer's term, an integration of the two combining gases. When, however, a liter of hydrogen is mingled within a liter of chlorine gas at the standard temperature and pressure, the two unite with violence by the action of sunlight, of flame, or the electric spark, and form two liters of chlorhydric acid gas; the first action of light, according to recent observations of Pringsheim, producing a sudden and transient increase of volume (due perhaps to a disintegration of the chlorine, which marks a stage in the chemical process).[1] The properties of the combining gases are lost in those of the new compound, but, contrary to the general law of chemical union, in which integration is attended by condensation, there is no loss of volume. We have in this case for the weight of a liter of the newly formed gas, not the sum of the weight of a liter of hydrogen and a liter of chlorine, but one half of that sum, or 18.25 times that of the liter of hydrogen.

8. Further light is shown upon this process by the history of the related fluorhydric acid gas, which at and near 100° has a density corresponding to HF. At about 19°, however, it is reduced to a liquid at the ordinary pressure, and between 20° and

[1] Pringsheim, L. E. D. Philos. Magazine, Dec. 1887, from Wiedemann's Annal. for Nov. 1887. The writer had already suggested that "the power of flame, or the electric spark, to effect the sudden union of chlorine and of oxygen with hydrogen, may be due to the effect of intense heat in separating momentarily into simpler forms portions of these gases, etc." (A New Basis for Chemistry, §57.)

30° yields, according to Mallet, a gas or vapor corresponding to H_2F_2, which by a slight elevation of temperature is readily transformed into 2HF. This gaseous compound of greater density is what in accordance with the general law of chemical integration should be formed by the union of H_2 with F_2, and we may conclude that in the case of chlorhydric acid a similar compound, H_2Cl_2, is possible, which, however, would at once pass, at the ordinary temperature and pressure, into 2HCl.

9. The capacity of the compound of fluorine and hydrogen to exist at the ordinary pressure in two gaseous states of unlike density serves to illustrate many similar facts in the history of elemental and compound species alike. Among the latter are the well known examples of acetic aldehyde, acetylene, pentine, and the various polymers of these. Among the elements, oxygen when liberated in the decomposition of water by fluorine (Moissan), or by electrolysis, appears in part in the gaseous modification known as ozone, having a density one and a half times that of the ordinary form of oxygen—that is to say, its weight is not sixteen times but twenty-four times that of hydrogen at the same temperature and pressure. The effect of the electric spark, and of the silent electric discharge, to convert a considerable portion of dry oxygen into ozone, which is, however, rapidly resolved by heat, and more slowly at ordinary temperatures into common oxygen, $2O_3 = 3O_2$; the case of selenium, which yields a condensed vapor, Se_8, resolvable at a higher temperature into Se_2; and that of the triply condensed sulphur vapor, S_6, now found to be convertible at higher temperature into S_2, corresponding to the normal oxygen, O_2; the vapors of phosphorus and arsenic, represented by P_4 and As_4, partially changed by heat into P_2 and As_2; and finally, the vapors of bromine and iodine, Br_2 and I_2, which alike by heat and by the explosive and silent electric discharge are more or less completely changed into unstable vapors of Br_1 and I_1—are all illustrations, then unknown, of the same principle of greater or less gaseous condensation, first advanced from theoretical considerations by the present writer in 1848 (§§2, 3). The fact that the silent electric discharge at a low temperature effects a similar disintegration in the vapors of bromine and iodine to that wrought by great heat or by the electric spark, thus producing a change apparently the reverse of that produced by the same silent discharge in oxygen gas, leads to the suggestion that the generation of ozone thereby may be

due to the momentary disintegration of a portion of oxygen, O_2, into 2O, which at low temperatures unites with an unchanged portion to form O_3.

The examples above given will suffice to show that the principle of chemical change by integration and disintegration appears not only in the relations of unlike species with each other, as of hydrogen with oxygen, with fluorine, with chlorine, or with sulphur and iodine vapors, but also with these same simple gaseous species among themselves. In other words, the more elemental gaseous forms of oxygen, of sulphur, of iodine, of fluorhydric acid, and of hydrocarbonaceous bodies, unite with themselves by homogeneous integration to form new gaseous species differing in specific gravity and in other physical characters, which have been designated allotropic or polymeric forms. Thus the same principle applies alike to the union of similar and dissimilar species, to homogeneous and heterogeneous integration, or, in the language long since adopted by the writer, to *chemical metamorphosis* as well as to *chemical metagenesis.*

10. We have seen that while the unit of weight is represented by the liter of hydrogen at 0° and 760 mm., the unit of combination for the derived species, such as water vapor and chlorhydric acid gas, is represented by twice this volume, the species being, in the language of Hofmann, dilitral. The corresponding dilitral volume of hydrogen gas itself then becomes $H_2=2$, a fact which is indicated by applying to it the term diad or diatomic. To this type of condensation also belongs nitrogen gas, together with oxygen, chlorine, and the vapors of bromine and iodine in their ordinary conditions, that of sulphur above 800° and of selenium above 1200°, that of tellurium, and probably that of antimony. Oxygen in the form of ozone, and selenium at low temperature, are triad or triatomic, while the ordinary vapors of phosphorus and arsenic are tetrad, apparently becoming diad at higher temperatures, and that of sulphur below 550° is hexad. Iodine vapor, as we have seen, may be metamorphosed into a monad species, in which its weight is not 127 times that of hydrogen gas at the same temperature, but one half that number; while the vapors of mercury and cadmium are known only in a monad form. A similar metamorphosis by expansion or homogeneous disintegration is, from analogy, possible for hydrogen at elevated temperature and reduced pressure; that is to say, the production

of a monad form of hydrogen, H, corresponding to monad cadmium vapor, Cd, and monad iodine vapor, I, and having for a liter at 0° and 760 mm. a weight of 0.0448 gram. Nor can we assign any reason *a priori* why the process of homogeneous disintegration may not go on still further, unless indeed it be limited by a process of heterogeneous disintegration which may resolve the hydrogen into two or more unlike species, as supposed by Grünewald to be the case in the solar chromatosphere.

11. The weight of a liter of water vapor is made up of that of a liter of diad hydrogen, H_2, with that of half a liter of diad oxygen; while the weight of a liter of chlorhydric acid gas includes only that of half a liter each of diad hydrogen and diad chlorine, or of a liter of monad hydrogen integrated with a liter of monad chlorine. Reasoning from compounds like this, it has been assumed that the weight of monad hydrogen, 0.0448 gram to the liter at standard temperature and pressure, is the smallest admissible, and that the weight of the element in a liter of any compound vapor or gas must be a multiple of this by some whole number; that of oxygen, if present, being in like manner not less than 7.98 times this same weight. The question arises whether we have as yet any experimental evidence of such homogeneous disintegration as should give in the liter of any vapor or gas at 0° and 760 mm., quantities of hydrogen or of oxygen not in accordance with these weights. In the vapor of ordinary water, in which the ratio by volume of $H : O = 100 : 50$, it is evident that there is no deviation from these values; but if, admitting the existence of an oxygenised water as described by Schützenberger, in which that ratio is 100 : 51 (1.0 : 8.14 by weight), we suppose this to be converted into a homogeneous vapor containing in a liter 0.0896 gram of hydrogen, it is evident that the oxygen, being not 0.0896×7.98 but 0.0896×8.14, will be equal to one and one-fiftieth portions. Further evidence of the distinctness of such oxygenised water, and of a similar oxygenised carbon dioxide described by Schützenberger, is however to be desired before the existence of such dissociation can be established.

12. We have now considered two kinds of chemical union: (1) heterogeneous integration, or the identification of volumes of unlike species, and (2) homogeneous integration, or the identification of volumes of like species, in which consists the so-called polymerisation and most cases of allotropism. Both of these

modes of union have a wide range, dependent on pressure; and the gaseous species formed by the first process become, like the elements themselves, the subjects of the second process. The process of integration by successive steps gives rise to homologous or progressive series, as in the paraffines, the olefines, the acetylenes, the benzenes, and other hydrocarbonaceous series, in recognised species of some of which the coefficient of the carbon is not less than 30. In the olefines, $n(CH_2)$, the first term being the same as the common difference, all the succeeding members of the homologous series are polymers thereof, constituting what we have called *isomeric homologues*. This name serves to distinguish them alike from those homologous series in which the first term is unlike the common difference, and which are *anisomeric homologues*, and from those isomeric compounds which are formed by successive homogeneous integrations, and between which, as between the allotropic forms of the elements, there is no apparent homology or similarity of function.

Familiar examples of such allotropic derivatives of species, themselves formed by heterogeneous integration, are seen in the successive condensations or homogeneous integrations of pentine, of acetylene, of cinnamene, and of the aldehydes, some of which take place spontaneously or with very slight provocation not only in gaseous but in liquid species. Besides the olefines among the hydrocarbons, we find in bodies like the carbon-spars, $n(CMO_3)$, examples of what must be regarded as isomeric homologues, and perhaps, though less apparently so, in the different allotropic forms of the titanium and silicon dioxides, wherein that similarity of function which marks homology is either non-apparent, from their chemical indifference, or else is absent. The latter is evidently the case in many cases of compounds the empirical formulas of which present good examples of progressive series, as in the metallic oxides, sulphides, and arsenides. An illustration of this is afforded in the observed compounds of manganese with oxygen, among which are MnO, Mn_3O_4, Mn_2O_3, Mn_5O_8, MnO_2, MnO_3, Mn_2O_7, and MnO_4, which, however, with but two exceptions, are known to us not in gaseous species, but only in highly condensed forms.

13. As the higher hydrocarbons of the various progressive series are built up by the integration of successive units of CH_2 with the first term of each series, so the monovalent alcohols and

the corresponding ammonias are generated in a similar manner from H_2O and NH_3. The capacity of such integration, or, in other words, the fixing power of such an integer as H_2, HCl, or NH_3, is very great, and theoretically knows no limit. By this consideration our conception of so-called atomicity or valency, which for an element has been defined as "its atom-fixing power measured by atoms of hydrogen" (J. P. Cooke), is greatly enlarged. Thus measured, chlorine is made monovalent, carbon tetravalent, and sulphur, like oxygen, divalent, although from its union with O_3 its hexavalence has been affirmed, a view which is sustained by the hexiodide of sulphur of Landolt, SI_6, and by the crystallised artificial sulphide of iron and nickel of Mackintosh (SFe_4Ni_5), while from the described iron sulphide, SFe_9, its octovalency would follow. Indeed, as there is reason to believe that the compounds of metallic iron formed in the blast-furnace with much smaller proportions of sulphur are homogeneous, it may be maintained that there is no limit to the valency of sulphur save that determined by the integral weight of the element on the one hand and that of the very highly condensed species known to us as molten iron on the other. Similar conclusions follow from the solution of carbon in the same metal, forming therewith compounds in which the hardness, fusibility, and magnetic relations of the metal are modified in a notable manner. The characteristic properties of the apparently homogeneous compounds of small proportions of both silicon and phosphorus, alike with iron, with copper and with other metals, and those of various metallic alloys, will at once suggest themselves to the chemist. In this connection may also be mentioned for illustration the solution of oxygen in molten copper, and that of the same gas in melted silver, forming a compound stable at high temperatures, but disintegrated on cooling at the ordinary pressure.

14. The power of fixing hydrogen possessed by various metals is not less instructive. The amount retained by palladium corresponds to Pd_2H, while potassium and sodium form therewith compounds of a certain stability, represented respectively by K_2H and Na_2H_2.[1] The capacity of the latter compounds to unite with smaller additional quantities of hydrogen, and that of other metals to combine with small amounts of the same element, show that the limit to be assigned to this power of fixing hydrogen by various metals presents as wide a range as that

[1] Troost and Hautefeuille, Comptes Rendus de l'Acad. des Sciences **28**, 968.

observed by the metals for sulphur, phosphorus, silicon, or carbon. The fixation of bodies in chemical union or solution is not the prerogative of one element rather than another, as the popular statement of the doctrine of valency would seem to imply. The question of the stability of a chemical compound, whether formed by homogeneous or by heterogeneous integration, is one of temperature and pressure; and heat, which readily effects the disintegration of the hydrides just mentioned, decomposes, either wholly or partially, at the atmospheric pressure, many metallic oxides. That the amount of one body retained in union with another is thus dependent on temperature, the pressure being constant, is well illustrated by the experiments of Spring on the arsenides of cadmium. The native metallic arsenides have for 100As quantivalent ratios for the metals represented by 33.3, 60, 66.6, 100, 150, 300 and 500, the latter $=1:5$ being generally regarded as representing the maximum fixing power or atomicity of arsenic, hence designated as pentavalent. When, however, cadmium is fused with an excess of arsenic at a low red heat, a large part of this is volatilised, and there remains a very hard metallic body giving essentially the ratio 1:6. It was not found possible to get by way of fusion a compound retaining a larger amount of arsenic, and this for the evident reason assigned by Spring, that "at the elevated temperature at which the combination of cadmium and arsenic takes place under ordinary pressure, the tension of dissociation is such that an arsenide is produced containing but little arsenic."[1] At ordinary temperatures, on the contrary, or under strong pressure, we have not to reckon with this tension of dissociation, and we readily get combinations containing a larger proportion of the volatile element. It is not the metal-fixing power of the arsenic, the oxygen, the sulphur, or the hydrogen, but rather the power of the metal to fix these more volatile elements under various conditions of temperature and pressure which we have to consider.

15. The ideal gas responds perfectly to external pressure, obeying implicitly Boyle's law; the ideal solid is, on the other hand, theoretically incompressible. Gas and solid are, however, alike expansible by heat, and this dynamic change of volume by thermic expansion, which is regular and constant, is thereby distinguished

[1] Formation de quelques arséniures métalliques par l'action de la pression. 1883. Proc. Roy. Acad. Belgique (3), 5, No. 2.

from changes of volume from chemical metamorphosis, which are periodic. Thus, at the standard pressure, water below 0° is a solid, while from 0° to 100° it is a liquid, and above this point a vapor, which, so far as observed, has, like the liquid, its own nearly constant rate of thermic expansion. The vapor of sulphur, however, which from 450° to 550° has a density ninety-six times that of hydrogen, assumes above 800° a density only thirty-two times that of hydrogen. In the case of iodine-vapor, and of the vapors of fluorhydric acid, of nitric peroxide, of acetic acid, of acetic aldehyde, of many hydrocarbons, and of solids which like arsenic, phosphorus, and tin undergo allotropic transformations, we see examples of the same periodic chemical changes.

16. The question of greater or less density of gas or vapor for elements, and for so-called polymeric species, as compared with that of the hydrogen unit, is a question of greater or less homogeneous integration. Moreover, the gaseous, liquid, or solid condition is theoretically wholly dependent on temperature and pressure, as pointed out in §6. It is known that liquid species, if not subject to heterogeneous disintegration by heat, pass thereby, under increased pressure, into vaporous forms far denser than the normal vapors, which, while having the character of condensed or polymeric species, are stable only within certain narrow limits, and alike by increase of temperature and by diminution of pressure are changed, through homogeneous disintegration, into less condensed vaporous species. The genesis and the transformations of these heavy vapors thus imply a chemical process analogous to that observed in the denser and lighter vapors of sulphur, iodine, fluorhydric acid, nitric peroxide, acetic aldehyde, and acetic acid.

W. Allen Miller long since pointed out that the dense vapors of ether and alcohol formed just above the critical points of these liquid species have tensions far less than belong to the normal vapors, and, moreover, that the abnormally dense vapors of these liquids on augmentation of temperature not only present a much greater rate of expansion than air or water vapor, but, instead of being like these constant therein, show a rapidly increasing coefficient of dilatation.[1] These phenomena, as we have elsewhere remarked,[2] are in accord with those presented by sulphur, which, near its point of condensation, yields a dense hexad vapor readily

[1] Miller. Chemical Physics, 3d edition (1863).
[2] A New Basis for Chemistry, 2d edition, §117.

disintegrated at a higher temperature (and doubtless also by reduced pressure) into a less dense diad vapor. Applying, then, Boyle's law to the tension of ether vapor as observed just above its critical point, we find it to be not the normal vapor, but a highly condensed polymer which, by increase of temperature, is metamorphosed into less and less condensed species, as shown by the very rapid increase of the elastic force as compared with that of air under similar conditions of temperature and pressure.

In illustration of this point we may note that Ramsay and Young have lately observed that the vapor of alcohol at 243° has a tension of only 63 atmospheres and a specific gravity of not less than .280, water being 1.000. This corresponds to a fourfold condensation, $4(C_2H_6O)$, since the normal vapor of alcohol calculated for that temperature and pressure should, according to Boyle's law, have a specific gravity of .0684, or but one fourth of the number observed.

17. The progressive stages which in sulphur, iodine, fluorhydric acid and acetic acid are marked in the process of homogeneous disintegration by heat at the ordinary pressure, do not, however, occur in the cases of ether, alcohol, water, and similar volatile liquids, except when these are heated under increased pressure; conditions under which all liquids not thereby exposed to heterogeneous disintegration may theoretically assume the gaseous state. The intermediate forms in the metamorphosis of volatile species are of very different degrees of stability, and while in many cases capable of existing at the ordinary pressure through a certain range of temperature, in others exist only within such narrow limits of temperature and pressure that we are led to conjecture from analogy that within still narrower limits there may exist many other intermediate species hitherto unknown and unsuspected. It may even be supposed that every variation in pressure acting upon compressible species gives rise to some passing chemical change too fugitive to be detected. It is known that variations in pressure control the production of allotropic forms in the case of solids, and may we not from analogy expect the same principle to apply in the action of pressure upon all bodies which depart from the theoretical elasticity of the perfect gas? The ideal gas responds perfectly to every variation of pressure, according to Boyle's law, while the ideal solid is on the contrary incompressible (§15), but the representatives of both of these can exist only within certain limits of temperature and pressure.

18. The seeming continuity of the liquid and the gaseous states of matter, as seen in the dense vapors discovered by Cagniard de Latour, and the fact that gaseous matter by successive condensations under great pressure assumes at high temperatures a condition not of liquidity, but of dense gas or vapor, as set forth by Andrews, receives a remarkable illustration in the discoveries of Hannay and Hogarth.[1] These chemists have found not only that solutions of salts in alcohol and ether have their critical points, above which they pass integrally into the state of dense vapors, but that the dense vapors of the solvent liquids themselves have, like condensed hydrogen gas, the power to take into solution various solids. The fact that water (and probably watery solutions also) will pass into the state of dense vapor not far from 400° (as long since shown by Cagniard de Latour), and that this vapor is, moreover, as found by the authors just cited, a solvent alike for silica, alumina, and zinc oxide, is one which throws great light on many problems in geogony and physiological mineralogy. It leads us to conclude that liquid water does not exist in highly heated rocks at considerable depths from the earth's surface, where, however, it may be present either in chemical combination, reducing their fusing point, as shown in the late researches of Tilden and Shenstone, or liberated, and pervading them as a dense vapor, holding dissolved mineral elements to be subsequently deposited as crystalline species. The above facts serve to show that a solution is really an integral chemical compound, in accordance with the view long maintained by the author.[2]

19. The law of volumes prevails in all known cases both of homogeneous and heterogeneous integration among gases and vapors, in the changes of oxygen, and of the vapors of iodine and sulphur, as in those of fluorhydric acid, of aldehyde, and of pentine and its polymers, as well as in the not less remarkable condensations or polymerisations of acetylene. All analogy leads us to extend this law to the still greater condensations observed in the denser vapors into which liquid species, above their critical points, are resolvable, and to the further condensation of the vapors into liquid and solid forms—to assume, in fact, that the law of combination by volume, like that of combination of weight (with which, so far as experiment goes, it is indissolubly linked), is universal.

[1] Hannay and Hogarth, Proc. Royal Soc. London **29**, 324, and Chemical News **12**, 103-106; also, A New Basis for Chemistry, 2d edition, §§120, 121.

[2] A New Basis for Chemistry, §12.

The coefficient of condensation in the case of gases and vapors is readily found by comparing the densities of the respective species at standard temperature and pressure, in the way well known to chemists; the weight of a given volume of hydrogen gas at that temperature and pressure being the unit. For the liquid and solid species formed by the homogeneous integration of these gases and vapors, as we have elsewhere endeavored to show, the weight of the same volume of the newly formed species at the temperature of its production under the standard pressure is to be taken as the term of comparison, either with that of the vapor or gas calculated for 0° and 760 mm., or finally, with the weight of an equal volume of hydrogen gas at the same temperature and pressure.

As declared by the writer in 1853, "the doctrine of chemical equivalents is that of the equivalency of volumes"; in other words, the law of volumes, like the law of weights, is universal, and for all species—liquid, solid, or gaseous—the volume, under proper conditions of temperature and pressure, is the same. The volume being then a constant quantity, the integral (or so-called equivalent or molecular) weight of any species, whether gaseous, liquid, or solid, is its specific gravity, hydrogen gas being unity.

20. The advantages to be gained by establishing a single unit for specific gravity, and by substituting alike for water at its maximum density (in the case of liquids and solids) and for air at 0° and 760 mm. (in the case of gases and vapors), hydrogen gas at the same temperature and pressure (a plan first indicated in the writer's volume entitled "A New Basis for Chemistry"), were urged in a paper entitled "Chemical Integration," read before the National Academy of Sciences in April, 1887, and published in the *American Journal of Science* for the following August. They were further insisted upon in a paper on "Integral Weights in Chemistry," read before the British Association for the Advancement of Science at Manchester, in September, 1887, and published in the *London, Edinburgh and Dublin Philosophical Magazine* for October of the same year. The integral weights of all gases and vapors are evidently their specific gravities, hydrogen being unity; and since water itself is the unit of specific gravity, adopted for convenience, for all liquids and solids, it becomes of the first importance to determine its integral weight. The weight of a liter of hydrogen gas (H_2) at 0° and 760 mm. being approximately 0.0896 gram, and

that of a liter of water at 100° (its temperature of formation at 760 mm.) 958.78 grams, we have:

$$0.0896 : 958.78 :: 2 : x = 21400.3.$$

Taking Regnault's figure for hydrogen = 0.089578 gram, the weight of a liter of water vapor ($H_2O = 17.96$) calculated for the same temperature and pressure = 0.8044 gram; we have then:

$$0.089578 : 958.78 :: 2 : x = 21406.6$$
$$0.8044 \quad : 958.78 :: 1 : x = 1191.9.$$

Of these, the last equation gives the coefficient of condensation for water, and if, rejecting the fraction, we assume water to be $1192(H_2O)$, we have $1192 \times 17.96 = 21408$. In the uncertainty which still prevails as to the exact weight of oxygen, hydrogen being unity,[1] we may safely assume in the calculation of their integral weights from the observed densities of other liquid and solid species, the first-found number, or 21400, as a sufficiently close approximation to the integral weight of water.

21. As regards the further history of the views just stated, it was pointed out in the first edition of the author's "New Basis for Chemistry" (§§66, 67) that in applying to water the well known formula for calculating the so-called atomic volume, $p \div d = v$, while d is its density at 4°, which is the unit of specific gravity for liquids and solids, p is the equivalent weight of its vapor, which is also its density, hydrogen being the unit. Hence the relation of $d : p$ involves the relation of the density of water to that of its vapor, and finally to that of hydrogen gas; and thus enables us to determine the amount of contraction of H_2O in passing from the gaseous to the liquid state, or, in other words, its coefficient of condensation, v being the reciprocal of this coefficient. It was then said, "the question to be settled in fixing the equivalent weight of water is to know its specific gravity as compared with hydrogen gas, or with steam."

In applying this method, the density of steam at 100° as compared with water at 100° having, for the reasons given, occupied the writer's attention, he, by inadvertence, took the densities at this temperature, and was thus led to assign to water the erroneous formula, $1628(H_2O)$, which, assuming $H_2O = 17.9633$, gave an integral

[1] *Vide* The Relative Values of the Atomic Weights of Hydrogen and Oxygen. Cooke and Richards, this Journal **10**, 81, and Proc. Amer. Acad. 1887, **23**; also Rayleigh, Proc. Roy. Soc. London, 1888, **43**, 356.

weight of 29244. In resuming, however, in §95 of the same volume, the question of the density of liquids and solids taken with water at 4° as unity, it was declared to be "necessary to refer them to a common standard of density, or, in other words, to determine the relation of density between water and hydrogen gas"; *d* being "the density of water at 4°, and *p* that of hydrogen at 0°." Soon after, in the paper on "Chemical Integration" referred to in §20, it was said that "instead of the weight of atmospheric air at 0° and 760 mm. . . . as the standard unit of specific gravity for all gases and vapors, hydrogen at the same temperature, which gives us the unit of integral weight, would seem to be the natural unit of specific gravity for all bodies whatsoever"; and again, in comparing the densities of liquid and solid species "with the density of the hydrogen unit, H_2, we get the specific gravity of these bodies, the diad integer of hydrogen at 0° and 760 mm. being unity." Still further, in the second paper cited in §20, it was said, "hydrogen, as the lightest known species, is the unit of integral weight in chemistry, and a liter of this gas at 0° and 760 mm. being assumed as a unit of volume for all species, the weight of a liter of any other vapor or gas at the standard temperature and pressure is its integral weight"; while the weight of the same volume for liquids should be taken "at the temperatures at which they are generated by the metamorphosis, through condensation, of the corresponding gaseous species." "In like manner, the weight of solids should, theoretically, be determined at the temperatures at which they are generated by the metamorphosis of gaseous or liquid species"; in other words, we should take for any solid species, "the weight of the same volume at the highest temperature at which that species can sustain without undergoing a change of state." Notwithstanding all these repeated statements, the erroneous value for the integral weight of water, calculated by comparing hydrogen gas, water vapor, and water itself, at the common temperature of 100°, was, by an oversight, retained until corrected by the writer in a note on "The Integral Weight of Water" in the *London, Edinburgh and Dublin Philosophical Magazine* for April, and in the *American Journal of Science* for May, 1888.

22. In the paper on "Integral Weights in Chemistry" was, moreover, considered at some length the relation of the regular thermic changes in volume alike of water and of most solid species to the question of integral weights and specific gravities. It follows from

what has been said above that, theoretically, the weight of the volume of water should be taken at 100°, and that of most solids, such as metals, ores, gems, and spars, at temperatures much more elevated. But we have sought to show by comparison of the cubic expansion of water between 4° and 100°, with the much smaller rates of expansion of the solid species in question between 4° and the temperatures of their chemical change by heat, that the resulting errors in the determination of specific gravities at ordinary temperatures to a considerable extent balance each other, and further, that the imperfections and impurities of most natural and artificial species introduce in such determinations "possible deviations in the one and the other direction as great as those due to the different rates of expansion of water and these species, so that we may take the approximate specific gravities got with water at 4° (or better, at 15.5°) as an available basis for fixing the integral weights of most solid species."

23. To illustrate alike the mode of calculating the integral weights of solid species, and the use and inter-relations of the two standards of specific gravity mentioned above, namely, water at ordinary temperatures and hydrogen gas at 0° and 760 mm., we may take the case of a crystalline species formed by the condensation of an unknown number of volumes of a theoretical calcium carbonate, $CCaO_3 = 100$. The integral weight of water being in round numbers (§20) 21400, and the specific gravity of the calcareous species (water 1.000) 2.730, we have $21400 \times 2.730 = 58422$. Dividing the integral weight thus found by that of $CCaO_3 = 100$, we find the number of volumes of this hypothetical carbonate condensed in one volume of the calcareous species, or, in other words, its coefficient of condensation, to be 584.22. Rejecting the fraction, we have for this species, which is calcite, $584(CCaO_3) = 58400$, with a theoretical specific gravity of 2.729.[1] The relation between the integral weight of the calcium carbonate $CCaO_3 = 100$ (hydrogen, 1.0, being unity) and the specific gravity of the calcite (water = 21400, being unity), is got by the equation

$$2.729 : 100 :: 1 : x = \frac{p}{d} = v = 36.643.$$

This, the so-called molecular or atomic volume of $CCaO_3$ as it

[1] The equivalent weight of $CCaO_3$ is here calculated with O = 16, substituting for which the value O = 15.96, we have instead of 100 the number 99.88. This gives for $584CCaO_3$, instead of 58400, an integral weight of 58330, corresponding to a specific gravity of 2.7357 instead of 2.7290, a difference so small that it may be neglected as within the limits of error.

"atomic linking" both single and double, forming "rings," "chain-like groups," "open chains," "closed chains," "branched chains," etc. Thus for example, "a branched series of atoms is obtained, composed of several linear chains. In the same way these branches can also divide, and the new branches may be united together by connecting links, forming ring-like or net-like structures." The author, however, tells us in a foot-note that the expression "ring-shaped" "need not be accepted as applying to space; it only indicates that the attractions between the atoms which maintain the coherence of the molecule form a continuous series."[1] In like manner Prescott states that "in the use of the chemical term, position," he will be understood to refer "not to arrangement in space, but to the order of the union of the atoms with each other."[2] Another distinguished American chemist has, however, lately assured us that the question of "atom-grouping has a mechanical as well as a chemical side," and notwithstanding the provisos above quoted, it seems impossible to divest the language which we have quoted from Lothar Meyer of a geometrical sense. Without speaking of the fancies of earlier writers as to the architecture of molecules, it is well known that Le Bel and Van't Hoff have speculated upon the supposed arrangement of the atoms of molecules in space, and that Wislicenus has lately made a further contribution in the same direction towards a hypothesis of the geometry of molecules.[3]

25. By such assumptions as the foregoing the modern atomistic chemistry seeks to explain the physical and chemical characters of species, which it regards as dependent upon forces and properties supposed to dwell in the individual atoms from which these are conceived to be built up. Structural formulas in accordance with this hypothesis may serve to explain the facts of definite and multiple proportions, of polymerism in vapors, and of the peculiar differences presented by such isomeric bodies as the primary, secondary and tertiary alcohols, $C_nH_{2n+2}O$. Assumed differences in "the order of the union of atoms with each other" may be made to account for the unlike genetic relations presented in their chemical changes by certain of these isomeric species, but there are other phenomena which it will require still further and purely

[1] All the expressions here quoted are from the chapter on the Law of Atomic Linking, in the late excellent translation by Bedson and Williams of the 5th edition of Lothar Meyer's Die Modernen Theorien der Chemie; Longmans, 1888.

[2] Prescott, "The Chemistry of Nitrogen," J. Am. Chem. Soc., Sept. 1887, 133.

[3] See this Journal **9**, 453.

gratuitous assumptions to explain by the atomic hypothesis. Such for example are the subtle differences which divide the amylic alcohol got by fermentation into two species, one optically active and the other inactive. These, though convertible the one into the other, present also minor chemical distinctions, and, moreover, transmit their optical characters to the derived valeric acids.[1] Similar chemical and optical unlikenesses appear in the limonenes, pinenes and camphenes, which are all apparently isomers of dipentine; and other examples of optical, crystalline and chemical differences meet us frequently in the study of isomeric and homologous bodies, which can hardly be explained by any constitutional or so-called structural formulas.

To indicate the essential differences which distinguish two substances having, it may be, the same centesimal composition and the same density, alike in the vaporous and the liquid or solid state, as in the instances above noted, they have been said by different writers to be unlike in "structure," or in "organization." The term structure, however, implies that the substance in question is put together or is built up by a certain arrangement of parts, while the term organization superadds the conception of such a subordination of parts to function as belongs to crystalline or to biotic structures. For these reasons it is conceived that the term "constitution," which implies no mechanical hypothesis, but simply refers to the character or the *essential form* of the species in question, is to be preferred. Chemical species are subject to constitutional changes, or, in the language of Andrews, to "internal disturbances," which alter to greater or less degrees alike their dynamical and their chemical relations. Such constitutional changes may manifest themselves in veritable metamorphosis by homogeneous integration or disintegration, and consequent change in integral weight; or in other cases by such slighter differences as have been signalised in the amylic alcohols and the various dipentines; or as are seen in certain cases of crystalline dimorphism, which are apparently independent of any change in density. Were it possible to establish on valid grounds the existence of chemical molecules, built up by the putting together of the atoms in the fantastic arrangements supposed by the present highly complicated atomic hypothesis, further assumptions would still be required to account for these minor constitutional differ-

[1] See on this subject the studies of Pasteur, Pedler, and Chapman and Smith; Watts's Dict. of Chemistry, 1st Supplement, *sub voce* Amyl Alcohols.

ences. Something radically different from this or any other mechanical hypothesis must, in the writer's opinion, be devised before we can hope to explain adequately the dynamical and chemical history of matter. Signs are not wanting that this famous hypothesis, so generally accepted by chemists since Dalton's time, is felt by many to be no longer adequate, and that, in the language of J. P. Cooke, it may be regarded as "only a temporary expedient for representing the facts of chemistry to the mind."[1] The fate which befell the corpuscular hypothesis of light, and now seems to menace the undulatory hypothesis, appears to await the atomic hypothesis in chemistry.

Contributions from the Laboratory of Cornell University.

VIII.—THE SAFETY OF COMMERCIAL KEROSENE OILS.

By Spencer B. Newbury and W. P. Cutter.

A series of experiments were made by the writers a year ago for the purpose of determining the maximum temperature reached by the oil in the reservoirs of the most powerful modern oil lamps. A brief outline of the results of these experiments was published in the *Scientific American Supplement*, July 16, 1887. The writers found that the oil in modern lamps often reaches a temperature of 110° to 112° F., and strongly urged the use in these lamps of oil having a high flashing point, in order to avoid danger of explosion.

The legal regulations in regard to the flashing point of illuminating oils vary greatly in different parts of the country, certain States having no statutes on the subject, others requiring that no oils shall be sold which do not reach a certain standard of safety. In New York State no oil is allowed to be sold which flashes below 100° F. when tested in the manner prescribed by law, in the instrument known as the New York State Tester. Most of the prevailing legislation upon the subject is probably based upon the observations of Dr. C. F. Chandler, who sixteen years ago made a careful study of the question of the safety of burning oils.[2] Dr. Chandler found that the oil in the lamps generally in use at

[1] American Journal of Science (1883) **26**, 310–316.

[2] Am. Chemist, Aug. 1872, 43.

that time, while burning in rooms at ordinary temperature, rarely reached 100° F., but nevertheless recommended the adoption of a legal standard of flashing point not lower than 120° F. In this connection he says,[1] "The point of 100° F. does not seem high enough to secure immunity from danger, though it may be said that very few, if any, accidents occur with oil which does not flash below this temperature."

If the standard of 100° was too low to afford protection with the old-fashioned single-wick burners, it must be far more inadequate at the present day when lamps are everywhere in use which raise the oil in the reservoirs to a point fully twenty degrees higher than that reached in the lamps which Dr. Chandler tested. In modern oil lamps with double wick or circular burner, the oil while the lamp is in use is often, probably generally, heated above its flashing point. It is evident, then, that the danger of explosion is constantly present while using these lamps with ordinary oils, unless, indeed, some other cause than temperature may contribute to the safety of oils which flash above 100°. It is not proved, for example, that the vapor of such oils can, at any temperature, form violently explosive mixtures with air. So far as previous experiments have shown, kerosene explosions may be due to the presence in oils of low flashing point, of small quantities of very volatile or gaseous hydrocarbons; these constituents may be absent in oils of high flashing test, these latter may therefore not be capable of exploding. In short, no clear statement has yet been made of the relation of the flashing point of oils to their capability of giving violent explosions with air. It was in the hope of establishing such a relation, and thus determining the value of the flashing point indications as a guarantee of safety, that the experiments described in this paper were undertaken.

The questions which presented themselves for study may be briefly stated as follows:

1. Will all the hydrocarbons of which burning oils are composed, when diffused in air in proper proportions, yield distinctly explosive mixtures? If so, at what temperature for each?

2. What are the most volatile constituents of ordinary kerosene, and how do the proportions of each of these lighter hydrocarbons affect the flashing point of the oil?

It is well known that it is difficult to produce explosive mixtures

[1] Johnson's Encyc., "Petroleum," 227.

of gases at will; the experiment of exploding marsh gas with air requires very careful adjustment of proportions, or no explosion results.

A series of hydrocarbons of nearly constant boiling point was obtained by careful purification and repeated fractional distillation of lighter petroleum products. The distillation was accomplished with the aid of a long Hempel tube. In testing the possibility of producing explosions with air with the several fractions, a strong glass cylinder 30 cm. high and with a capacity of 300 cc. was employed. This was immersed nearly to its mouth in a water-bath, by means of which the experiments could be made at any desired temperature. The amount of each hydrocarbon which could be completely burned by this volume of air was calculated, and the corresponding quantity of each fraction weighed out in a thin glass bulb about ½ cm. in diameter. When a test was to be made, a little mercury was placed in the cylinder, the little bulb of hydrocarbon introduced, and the cylinder closed by a well-fitting stopper. By shaking, the bulb was then broken and its contents diffused throughout the air in the cylinder. The explosiveness of the mixture was tested by cautiously removing the stopper and applying a small flame to the mouth of the jar. The experiments were made with varying qualities of each hydrocarbon, and at different temperatures. It was found that the most violent explosions were obtained by the use of nearly the amount of the hydrocarbon which could be completely burned to water and carbon dioxide by the volume of air in the cylinder. It was shown at once, moreover, to the surprise of the experimenters, that sharp explosions could be obtained at ordinary temperatures with hydrocarbons of comparatively high boiling point, as for example with heptane, which boils at about the same point as water. The following table gives a summary of the results obtained:

Hydrocarbon.	Formula	B. P.	Source.	B. P. of Fraction.	Temperature at which explodes with air.
Butane . . .	C_4H_{10}	1° C.	C_2H_5I and Sodium.	1° C.	Ordinary.
Pentane (Iso) .	C_5H_{12}	30°	Petroleum Ether.	30°	"
Hexane . . .	C_6H_{14}	68°	" "	67–68°	"
Heptane . . .	C_7H_{16}	98.5°	"Abietene" (*Pinus Sabiniana.*)	98.5°	"
Octane . . .	C_8H_{18}	124°	Illuminating Oil.	125-130°	"
Nonane . . .	C_9H_{20}	149.5°	" "	148-150°	Between 150° and 212° F.
Decane . . .	$C_{10}H_{22}$	161° (?)		160-165°	Between 150° and 212° F.

Nonane and decane could not be made to explode with air at temperatures under 150° F., but by heating the bath to 212° F. distinct explosions were obtained. As these hydrocarbons seemed to mark the limit of the constituents of a safe oil, experiments were made under conditions similar to those which prevail in a burning lamp. A cylindrical copper vessel of about 300 cc. capacity was employed, provided with a loosely fitting cover through which a hole about $\frac{3}{16}$ inch in diameter had been bored. This was charged with a few drops of the material to be tested, and gradually heated in a water-bath, a small flame being applied to the orifice from time to time, as in the ordinary method of testing oils. The point of explosion was shown by a distinct puff which threw off the cover of the vessel. The results were more definite than those obtained by the use of the glass cylinder, and show that the legal limit as to flashing point lies between these two hydrocarbons.

Nonane exploded sharply at 79° F.
Decane " " " 104° F.

A sample of illuminating oil which showed a flashing point of 111° F. by the New York State tester gave, when tested as above, a distinct explosion at that temperature, 111° F.

The above experiments lead to the following conclusions:

1. All the paraffines up to decane, and probably also higher members of the series, may at suitable temperatures form explosive mixtures with air.

2. Oils which flash at a point considerably above the legal requirement may, under proper circumstances, give violent explosions at their flashing temperature.

3. An oil consisting of pure decane, $C_{10}H_{22}$, would be accounted a safe oil by the legal flashing point test of New York State, while one consisting of nonane would be below the standard.

In order to determine what are the lowest hydrocarbons present in ordinary burning oil, a sample of commercial "water-white" oil of excellent quality, showing a flashing point of 108° F., was carefully distilled, at first in a vacuum, and the lighter portions repeatedly fractionated by means of a Hempel tube. Two kilograms of oil yielded 30 grams of a distillate boiling at 110°–130° C., which on further rectification proved to be chiefly octane; and 100 grams, boiling at 130°–160° C., which appeared to consist principally of nonane and decane. Only traces of hydrocarbons

of lower boiling point than octane were present. The addition of 5 per cent. of heptane to a sample of this oil lowered the flashing point to 97°. A specimen of "mineral sperm" oil which flashed above 212° F. was treated with different proportions by weight of pentane, hexane, and heptane, and the reduction of the flashing point noted.

Mixtures of Mineral Sperm Oil with Light Hydrocarbons.

Mineral sperm oil	95	per cent.,	pentane	5	per cent.,	flashes	110° F.
"	"	"	90	"	"	"	10	"	"	"	ord. temp.
"	"	"	95	"	"	hexane	5	"	"	"	110° F.
"	"	"	90	"	"	"	10	"	"	"	ord. temp.
"	"	"	95	"	"	heptane	5	"	"	"	145° F.
"	"	"	90	"	"	"	10	"	"	"	110° F.
"	"	"	83	"	"	"	15	"	"	"	96° F.
"	"	"	80	"	"	"	20	"	"	"	ord. temp.

It is evident, therefore, that the low flashing point and danger of oils may be due not to the presence of small quantities of very volatile products, but rather to the large proportion which they contain of constituents of moderately high boiling point.

The burning test which determines the temperature at which a sample of oil may be set on fire and will burn in an open vessel, has been generally conceded to be unreliable as an indication of safety. Nevertheless, the laws of New York State prohibit the sale of oil which burns below 300° F. An oil may show a very high burning test and yet be of low flashing point and therefore extremely unsafe. This is especially the case with oils which consist of a mixture of very heavy and very light hydrocarbons. The more nearly homogeneous an oil is in composition the closer the flashing and burning points will approach each other. For example, the fractions corresponding to nonane and decane used in the experiments described above take fire at a temperature but little above their flashing points.

Nonane flashes 79° F., burns 110° F.
Decane " 104° " " 136° "

The flashing point of an oil is also, as is well known, dependent not only on the proportion of light constituents present, but upon the character of the oil as a whole. An unsafe oil may be brought up to legal standard by adding to it a sufficient quantity of heavy lubricating oil, but such a heterogeneous mixture will be of poor quality for burning purposes. It is doubtless this which has led manufacturers to make the oft-repeated claim that a high flashing

point is inconsistent with good burning qualities. If refiners would be content to make a little less oil, leaving out some of the benzine and some of the lubricating oil as well, there would be no difficulty in producing illuminating oils of high flashing point and excellent illuminating power. The well known Astral oil, which flashes at 125° F., is a standing protest against the claim of superior burning qualities for low-grade oils. This is simply the *heart* of the burning oil freed from both lighter and heavier deleterious ingredients. Tests made by the authors have shown that the above mentioned brand burns admirably in modern lamps, and by photometric tests gives results fully equal to any other oil in the market.

We are at present engaged in a series of experiments to determine the relative value as illuminating agents of the different hydrocarbons composing kerosene. The results of these experiments will form the material of another communication.

Only a very small amount of volatile material requires to be removed from an oil of ordinary character in order to raise its flashing point materially, as the following experiment shows.

One kilogram of an oil flashing at 108° F. was placed in a flask, and a gentle current of air at ordinary temperature aspirated through it during 24 hours. At the end of that time the oil was found to have lost 28 grams, or 2.8 per cent. in weight, and showed a flashing point of 116° F. Treatment of ordinary oils by a somewhat similar process would doubtless be effective in making them materially safer, and would probably add but a fraction of a cent per gallon to their cost.

It would be too much to expect of refiners that they should furnish oils of much higher flash test than they are required to do by law. The passage of a statute raising the legal standard to 120° would, however, cause no serious hardship to manufacturers, and would effect a saving of life and property which would far outweigh the very slightly increased cost of burning oil. It has been urged that with such a law manufacturers would simply add heavier products to their oils and thus bring them up to the legal standard, to the detriment of their burning qualities. This would, however, be in opposition to their own interest, since oils of high flash and excellent quality are already in the market and are extensively used.

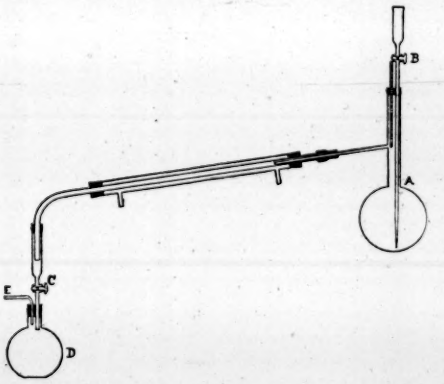
The experiments described above show conclusively that an oil heated above its flashing point is dangerous, whether that point be

high or low. There can, therefore, be no doubt that in using kerosene of ordinary quality in the powerfully heating lamps which are now common, we are dependent for our safety upon the accurate construction of the burners, which render it difficult for the explosive vapors in the lamp to become ignited. An oil which flashes below 120° F. is not safe to use in these lamps, and with oils of ordinary grade the conditions of explosion are constantly present.

IX.—APPARATUS FOR FRACTIONAL DISTILLATION IN VACUUM.

By Spencer B. Newbury.

The subject of distillation under reduced pressure has been thoroughly discussed by Anschütz,[1] and the apparatus recommended in that author's pamphlet certainly appears to leave little



to be desired in respect of convenience or efficiency. The arrangement shown in the accompanying figure has, however, the advantage that none of its parts require to be specially constructed, and the whole may easily be put together from apparatus to be found in almost any laboratory.

[1] Ueber die Destillation unter vermindertem Druck, Bonn, 1887.

A distilling bulb, *A*, is provided with a double-bored rubber stopper, through one aperture of which passes a thermometer, and through the other the tube of an ordinary separating funnel, drawn out at its lower end to a capillary tube which reaches nearly to the bottom of the flask. The outlet tube of the bulb is connected with a condenser, as shown in the sketch. The inner tube of the condenser is bent down at its lower end and terminates in a second separating funnel, the tube of which passes into the receiver *D*; from the latter a small bent tube *E* serves to connect the apparatus with an ordinary Bunsen filter-pump provided with a manometer.

The substance to be distilled is placed in *A*, the air exhausted to constant pressure, and the distillation commenced by heating *A* in a bath of water or paraffine. A gentle current of air is allowed to bubble through the liquid by slightly opening the stop-cock *B*; this may be so slight as to have no effect on the pressure, and serves to prevent the "bumping" of the liquid. As soon as one fraction has been collected in the receiver the stop-cock *C* is closed, air is admitted through *E*, and the flask *D* removed and replaced by another. This is then emptied of air, the stop-cock *C* opened, and a second fraction collected. In this manner a series of fractions may be obtained without the necessity of admitting air to the whole apparatus when the receiver is changed. (This is essentially the arrangement described by Thörner.[1])

The separating funnel *B* serves not only as an inlet tube for air, but also for the introduction of the successive fractions for redistillation without loss of vacuum. By the use of this simple device complete fractional distillation may be effected almost as rapidly and uninterruptedly as under ordinary pressure.

X.—ON THE DECOMPOSITION OF ACETONE WITH BLEACHING POWDER.

By W. R. Orndorff and H. Jessel.

In the Annalen der Chemie, Vol. I, page 199, Liebig, after mentioning the formation of chloroform by distilling dilute alcohol with calcium hypochlorite, states that chloroform may also be obtained, and in greater quantity, if acetone be treated with calcium

[1] Ber. d. chem. Ges. **19**, R. 467.

hypochlorite, under the same circumstances. No other reference to the formation of chloroform from acetone occurs in the literature, if we except the statement of Siemerling[1] that the use of acetone for the preparation of chloroform is not advantageous, because the price of it is high and the product does not exceed one third of the acetone used. Notwithstanding Siemerling's statement, it has been found very advantageous to use acetone in the manufacture of chloroform, and at the present time a large amount of chloroform is actually made by the very method that Siemerling condemned. As there was nothing in the literature concerning the reaction which takes place when acetone is decomposed with bleaching powder, the present investigation was undertaken for the purpose of throwing some light on this subject.

The acetone used was a commercial product, boiling from 58° to 60° C. This was first dried over calcium chloride and then fractioned with a Hempel tube. The larger part of the acetone came over between 56° and 58° C., and this was used in all of the experiments. The bleaching powder was also a commercial article, and contained thirty-three and one third (33⅓) per cent. of available chlorine. The apparatus used consisted of a four-liter balloon flask provided with a three-hole rubber stopper. Through one of the holes passes a separatory funnel reaching to the bottom of the flask. The second hole has a glass tube of tolerably large diameter, which also reaches to the bottom of the flask. Through the third hole passes the exit tube, which is collected with a Liebig's condenser. The bleaching powder is placed in the flask together with the requisite amount of water. A weighed quantity of acetone, after having been diluted with a certain quantity of water, is then gradually added through the separatory funnel. The reaction begins spontaneously, and the chloroform distills without the application of external heat. After all the acetone has been added, and the heat of the reaction has somewhat subsided, the flask is placed on a water-bath and the bath heated. Steam is now passed through the mixture in the flask so as to drive out all the chloroform. The flask must be shaken while the acetone is being added, and care must be taken not to add the acetone too fast, otherwise the flask becomes very hot and the mass is apt to froth over, owing to the chloroform distilling too rapidly. After a long series of experiments the following proportions were found to

[1] Arch. for Pharm. Trier [2] **53**, 23.

give the best results: 275 grams of bleaching powder (33⅓ per cent. available chlorine) were mixed in the flask with 800 cc. of water; 22 grams of acetone were then diluted with 70 cc. of water and gradually added through the separatory funnel. The yield of chloroform amounts to 166 to 173 per cent. of the weight of the acetone used. The chloroform obtained by this method was found to be very pure, and after being washed and dried, boiled constantly at 61.5°, and had the specific gravity 1.5263 as compared with water at 4°.

The residues left in the flask in a long series of experiments were united and filtered. The solid material left on the filter was examined and found to be almost entirely calcium hydroxide, together with a small amount of calcium hypochlorite and calcium carbonate. Through the clear filtrate carbon dioxide was passed to remove the calcium hydroxide in solution, then it was filtered and the filtrate treated with a concentrated solution of potassium carbonate as long as any calcium carbonate was precipitated. The precipitated calcium carbonate was then filtered off and the solution of the potassium salts evaporated to crystallisation. Two kinds of crystals were obtained, cubical crystals of potassium chloride, and needle-shaped crystals which appeared to be potassium acetate. Most of the potassium chloride was separated by fractional crystallisation from water. The mother-liquors were then evaporated to dryness on the water-bath and the dry mass treated with alcohol (95 per cent.), in which potassium acetate is very soluble and potassium chloride almost insoluble. The alcoholic solution was filtered and the filtrate evaporated to dryness on the water-bath. The dry mass was very deliquescent and absorbed moisture enough from the air to dissolve completely if allowed to stand unprotected. Treated with alcohol and sulphuric acid and distilled, acetic ether was formed. With a solution of ferric acetate it gave the characteristic precipitate of basic ferric acetate. A hot saturated solution, when treated with a strong solution of silver nitrate, filtered and allowed to cool, gave the characteristic flat needle-shaped crystals of silver acetate. These were separated, recrystallised from water, dried, and analysed with the following results:

	Found.	Calculated for $Ag(C_2H_3O_2)$.
	64.47	64.67
Ag	64.57	

From these results it will be seen that the products formed by the action of bleaching powder on acetone are chloroform, calcium hydroxide, calcium chloride, and calcium acetate.

It is probable that the first action of the bleaching powder is a substituting one, yielding trichloracetone or methyl chloral, according to the equation,

$$2CH_3COCH_3 + 6CaOCl_2 = 2CH_3COCCl_3 + 3Ca(OH)_2 + 3CaCl_2.$$

This methyl chloral is then acted on by the calcium hydroxide formed at the same time, and chloroform and calcium acetate are formed thus:

$$2CH_3COCCl_3 + Ca(OH)_2 = 2CHCl_3 + Ca(C_2H_3O_2)_2,$$

or, combining the two equations,

$$2CH_3COCH_3 + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + Ca(C_2H_3O_2)_2.$$

This equation requires for one molecule of acetone one of chloroform, or a yield of 206 per cent. of the weight of acetone used. The best yield obtained in the factory is 188 per cent. The amount of bleaching powder required by this equation agrees very well with the amount found by experiment to give the best results.

In the Annalen der Chemie, Vol. I, page 228, Liebig says that if acetone be warmed slightly with a solution of calcium hypochlorite, a strong precipitate of *calcium carbonate* is formed, and on distillation, chloroform passes over. As this statement is a direct contradiction of the above equation and the facts from which it was derived, a clear solution of bleaching powder was prepared by treating bleaching powder with water and filtering the solution, and then heated with a small quantity of acetone. A strong precipitate was thrown down at once, and the odor of chloroform was distinctly perceptible. The precipitate was filtered off and examined and found to be *calcium hydroxide*, and not *calcium carbonate* as stated by Liebig, thus confirming the results obtained above. Acetophenone ($C_6H_5COCH_3$), treated in the same way, caused the clear solution of bleaching powder to become clouded, owing to the precipitation of calcium hydroxide. On distillation, chloroform passed over, calcium benzoate was found in the flask from which the chloroform was distilled. In this case probably trichloracetophenone or phenyl chloral is first formed thus:

$$2C_6H_5COCH_3 + 6CaOCl_2 = 2C_6H_5COCCl_3 + 3Ca(OH)_2 + 3CaCl_2,$$

and this, with the calcium hydroxide formed at the same time, gives chloroform and calcium benzoate, thus:

$$2C_6H_5COCCl_3 + Ca(OH)_2 = (C_6H_5COO)_2Ca + 2CHCl_3.$$

Bischoff[1] and Cloëz[2] have shown that when acetone is treated with chlorine, trichloracetone or methyl chloral is the final product; and both Krämer[3] and Morawski[4] have demonstrated that trichloracetone heated with a solution of an alkali yields chloroform. In order that there might be no doubt about this matter, acetone was treated with chlorine in the sunlight until it would absorb no more chlorine. The heavy oily product was then distilled with milk of lime, and chloroform was found in the distillate. Lieber[5] after giving a list of the substances which give the iodoform reaction when treated with iodine and caustic potash, states that all these bodies contain the methyl group, and that "man kann sich den Hergang bei der Reaction etwa so vorstellen, das KOH daran theilnimmt, indem H mit dem sich abspaltenden CH_3 und KO mit dem Rest in Verbindung tritt, während zugleich das Jod substituirend wirkt und so Jodoform bildet. Die Reaction findet nur dann statt wenn der vom CH_3 abgespaltene Rest geeignet ist, mit KO in Verbindung zu treten, d. h. entweder ein Säureradical ist, oder doch leicht sich durch Oxydation in ein solches verwandelt."

In the light of the results on the formation of chloroform from acetone and bleaching powder, it would seem that the formation of iodoform is in all respects analogous to the formation of chloroform, *i. e.* that the iodine first acts as a substituting agent, giving a tri-iodo substitution product, and that this breaks up in the presence of the alkali, yielding iodoform and an acid residue which unites with the caustic alkali. The above process of making chloroform from acetone might well be substituted for the one ordinarily given in text-books on organic chemistry, in which alcohol and bleaching powder are used. The yield of chloroform is much better, the process quicker and more satisfactory, and the explanation of the reaction, if anything, simpler.

[1] Ber. **8**, 1339.
[2] Ann. chim. phys. [6], **9**, 145.
[3] Ber. **7**, 258.
[4] J. prak. Chem. 1875, 388.
[5] Ann. Chem. Sp. Bd. **7**, 230.

XI.—ON THE DECOMPOSITION OF SOME DIAZO COMPOUNDS IN FORMIC AND ACETIC ACIDS.

By W. R. Orndorff.

The study of the decomposition of some of the simplest diazo compounds in formic acid was undertaken with the hope of realising the following equation:

$$C_6H_5N=N.NO_3 + HCOOH = C_6H_6 + N_2 + HNO_3 + CO_2.$$

This reaction, if successful, would then furnish us with an easy means of replacing the amido group by hydrogen, and could be substituted for the decomposition of diazo compounds with alcohol, which has been shown not to be always reliable. It was soon found, however, that the reaction was of an entirely different character. No carbon dioxide was evolved, though decomposition took place readily and the N_2 group was driven out. Esters of formic acid seemed to have been formed, though it was impossible to prove this, owing to the fact that phenyl and cresyl formates decompose when distilled with steam or when heated to their boiling point. Since it was found impossible to isolate the first products of the decomposition of the diazo compounds with formic acid, acetic acid was substituted for formic acid.

Decomposition of diazo-benzene nitrate with glacial acetic acid.—The diazo-benzene nitrate was made according to the method of Griess, filtered off with the aid of the pump, washed with absolute alcohol and then with anhydrous ether, and finally spread out upon drying paper and allowed to remain until all the ether had evaporated. The white crystallised salt was then placed in a vacuum desiccator over sulphuric acid and allowed to remain until thoroughly dry. About 10 grams of the dry diazo-benzene nitrate were decomposed at a time. This quantity was placed in a liter Erlenmeyer flask and 100 cc. glacial acetic acid added. The flask was then placed in a water-bath and the bath heated. The diazo-benzene nitrate dissolved quite readily in the hot acetic acid and imparted to it a slightly yellowish red color. On continuing to heat until the water in the bath was about 70° C., nitrogen gas began to escape through the liquid. The lamp was then removed and the decomposition allowed to proceed. It was found that the decomposition was best effected at as low a temperature as possible, and if at any time the action became too violent it was

checked by dipping the flask in cold water. When the gas ceased to come off, the water in the bath was kept boiling for some time to insure the complete decomposition of all the diazo-benzene nitrate. The glacial acetic acid became deep red in color. The gas evolved was collected, examined, and found to be nitrogen. About 200 grams of the dry diazo-benzene nitrate were decomposed in this way in 10-gram portions. The portions of the red colored liquid left in the flask after each decomposition were poured together and the resulting liquid diluted with about ten times its bulk of water. A dark red colored oil separated out. After standing for some time this was collected, placed in a round-bottom flask with some water, and distilled in steam in order to free it from tarry impurities. It was then washed several times with a very dilute solution of sodium hydroxide, and finally dried over calcium chloride and subjected to fractional distillation. A colorless oil was obtained which boiled constantly at 195° C. (Anschütz thermometer, entirely in vapor; bar. 733 mm.) On analysis this oil gave the following results:

	I.	II.	Calculated for $C_8H_8O_2$:
C	70.77	70.66	70.59
H	6.07	6.17	5.88

A small portion of the oil, when boiled with a strong solution of caustic potash, dissolved, and acetic acid and phenol were found to be present in this solution. These results show that the substance is undoubtedly phenyl acetate. The decomposition of diazo-benzene nitrate in glacial acetic acid therefore takes place in accordance with the equation,

$$C_6H_5N_2NO_3 + CH_3COOH = CH_3COOC_6H_5 + N_2 + HNO_2,$$

the products being phenyl acetate, nitrogen and nitric acid. This equation is analogous to that by which phenetol is formed by the action of alcohol on diazo-benzene nitrate,

$$C_6H_5N_2NO_3 + HOC_2H_5 = C_6H_5OC_2H_5 + N_2 + HNO_3.$$

The yield of phenyl acetate is very small, owing to the fact that much tar is formed.

Phenyl Acetate.—This substance was first made by Cahours,[1] by the action of acetyl chloride on phenol. It has since been investigated by Scrugham,[2] Broughton,[3] Guareschi,[4] and by Perkin and Hodgkinson.[5] Different investigators have given it different boil-

[1] Ann. Chem. **92**, 316. [2] Ann. Chem. **92**, 317. [3] Ann. Chem. Spl. Bd. **4**, 121.
[4] Ann. Chem. **171**, 142. [5] J. Chem. Soc. **37**, 487.

ing points, from 188° (Scrugham) to 200° (Broughton). Phenyl acetate was therefore made by treating pure phenol with a slight excess of acetyl chloride, heating the flask, connected with an air condenser, for some time until all the hydrochloric acid is driven off. The liquid remaining in the flask was then subjected to fractional distillation and the greater part was found to boil constantly at 195°. The thermometer used was an Anschütz standard thermometer and the mercury column was entirely surrounded by vapor. (Bar. 733 mm.) Phenyl acetate thus made is identical in all respects with that obtained by the decomposition of diazo-benzene nitrate with glacial acetic acid. It is a peculiar-smelling liquid, the odor lasting for some time. It is perfectly colorless when pure, and does not become colored on standing, provided it be perfectly pure (cf. Broughton). It is only very slightly soluble in water, to which it imparts its characteristic odor. It is soluble in ether, chloroform, alcohol, strong formic and glacial acetic acids. From the solution in formic and acetic acids it is precipitated on dilution with water. Benzene and petroleum ether dissolve it only when used in large excess. It is readily saponified when boiled with solutions of the caustic alkalies, forming acetates and phenolates. It is not decomposed by boiling water, and is readily volatile with steam. The specific gravity of phenyl acetate as determined by Broughton is 1.074. A determination of the specific gravity of the phenyl acetate made by the decomposition of diazo-benzene nitrate in glacial acetic acid as well as of that made from phenol and acetyl chloride, using Perkin's modifications of the Sprengel specific gravity tube,[1] gave 1.0927 at 0° as compared with water at 4°C. One of the curious things about phenyl acetate is that its index of refraction being very nearly the same as that of German fusible glass, a piece of this is invisible when placed in the clear colorless fluid. This fact was first noted by Broughton.

Decomposition of p-diazo-toluene sulphate with glacial acetic acid.—*p*-Diazo-toluene sulphate was made and dried according to the method already given.[2] The perfectly dry white crystallised salt was then placed in a flask with glacial acetic acid and decomposed, using the same proportions, method, and precautions as in the case of the decomposition of diazo-benzene nitrate. Altogether about 300 grams were decomposed in 10-gram portions. The residues left in the flask were united and diluted with ten

[1] J. Chem. Soc. **45**, 444. [2] Am. Chem. J. **9**, 387.

times the volume of water. The oil which separated out was then collected, distilled in steam to free it from impurities, washed two or three times with a very dilute solution of caustic soda, dried over calcium chloride and subjected to fractional distillation. A pleasant-smelling colorless oil was obtained which boiled constantly at 213° C. (Anschütz standard thermometer, entirely surrounded by vapor; bar. 734 mm.) On analysis this oil gave the following results:

	I.	II.	Calculated for $C_9H_{10}O_2$.
C	72.14	71.92	72.00
H	6.67	6.68	6.66

It readily dissolved when boiled with a strong solution of caustic potash, and both para-cresol and acetic acid were found in this solution. A determination of the specific gravity with Perkin's specific gravity tube gave 1.0658 at 0° C. as compared with water at 4° C. From these results it will be seen that the reaction which takes place is represented by the equation

$$C_6H_4\begin{matrix}CH_3\\ N_2HSO_4\end{matrix} + CH_3COOH = CH_3COOC_7H_7 + H_2SO_4 + N_2,$$

cresyl acetate, $CH_3COOC_7H_7$, being formed. The yield of cresyl acetate is very small, probably owing to some secondary reaction between the cresyl acetate and the sulphuric acid.

p-Cresyl Acetate.—This substance was first made by Fuchs,[1] and described by him as a yellow fluid having a disagreeable odor and boiling at 208°–211°. Perkin and Hodgkinson[2] also describe a cresyl acetate which they made by treating cresol (obtained from Kahlbaum) with acetyl chloride. This, they say, is a beautiful colorless fluid, boiling at 214°; but as they do not state whether their cresol was the ortho, meta, or para compound, it is impossible to say whether their cresyl acetate was identical with that of Fuchs or not. Fuchs used the para-cresol, and therefore his cresyl acetate was undoubtedly the para compound. In order to determine accurately the boiling point and properties of *p*-cresyl acetate, and to compare it with the substance obtained by the decomposition of *p*-diazo-toluene sulphate with glacial acetic acid, pure *p*-cresol (m. p. 36°) was treated with a slight excess of acetyl chloride, and heated in a flask connected with an air condenser until all the hydrochloric acid was driven off. The liquid was then subjected to fractional distillation, and the larger part was found

[1] Ber. **2**, 626. [2] J. Chem. Soc. **37**, 489.

to boil constantly at 213°. (Anschütz thermometer, entirely surrounded by vapor; bar. 734 mm.) Thus made, cresyl acetate is a colorless oil, highly refracting, having a pleasant odor when pure, but an exceedingly disagreeable one in the impure state. It is but slightly soluble in water, and readily volatilises with steam without undergoing any decomposition. It is soluble in alcohol, ether, chloroform, in formic and acetic acids, and in large excess of benzene and petroleum ether. From its solution in formic and acetic acids it is precipitated on dilution with water. The specific gravity of the *p*-cresyl acetate made from *p*-cresol and acetyl chloride was determined very accurately by means of a specific gravity U tube (Perkin's modification of Sprengel's sp. gr. tube), and found to be the same as that already determined for the *p*-cresyl acetate made by the decomposition of *p*-diazo-toluene sulphate with glacial acetic acid, viz. 1.0657 at 0° C. compared with water at 4° C. From these results it will be seen that the cresyl acetates from the two sources are undoubtedly identical.

The *p*-diazo-benzene-sulphonic acid of Schmitt[1] was made according to the method of Fischer[2] and decomposed in glacial acetic acid. Much nitrogen was evolved and the liquid became colored a deep red. After evaporating off all the acetic acid on the water-bath, a syrupy liquid remained which had acid properties and appeared to be the *p*-acetyl-phenol-sulphonic acid, $C_6H_4<^{OOCCH_3}_{SO_3H}$. Owing to lack of time nothing further was done with this compound. Meldola[3] has recently shown that the same reaction takes place in the naphthalene group. He obtained *m*-nitro-benzene-azo-acetyl-β-naphthol by treating *m*-nitro-benzene-azo-β-naphthylamine with glacial acetic acid and sodium nitrite. It may therefore be assumed that the reaction between diazo compounds and glacial acetic acid is a general one for all diazo compounds. The only other reference to such a reaction in the literature is a statement of Hayduck[4] that when diazo-*o*-amido-*p*-toluene-sulphonic acid, $C_6H_3\left\{\begin{matrix}CH_3\\N_2\\SO_3\end{matrix}\right>$ was decomposed with glacial acetic acid, it gave an acid containing the acetyl group and which formed crystallisable salts with bases. The reaction, however, he says, is not simple, and here he leaves the work.

[1] Ann. Chem. **120**, 144. [2] Ann. Chem. **190**, 76.

[3] Ber. **21**, 601. When Meldola published his preliminary notice in the Berichte, the work described in this paper was nearly completed. [4] Ann. **172**, 217.

Contributions from the Chemical Laboratory of Harvard College.

LXI.—ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

By Henry B. Hill and Arthur W. Palmer.[1]

On Sulphopyromucic Acids.[2]

Pyromucic acid shows in many of its reactions so close an analogy to benzoic acid that a study of its behavior toward concentrated sulphuric acid could hardly fail to yield interesting results. In 1860 Schwanert[3] prepared a sulphopyromucic acid by distilling sulphuric anhydride slowly over powdered pyromucic acid. The barium salt was said to be not distinctly crystalline, and its composition was established by a single determination of barium in the salt dried at 150°. With the exception of the brief notice by Schwanert, we have been able to find no mention of furfuran derivatives containing the sulpho group. We have found that a sulphopyromucic acid is formed without difficulty when pyromucic acid is dissolved in fuming sulphuric acid, and that a second sulphonic acid may readily be made by indirect methods. We have also prepared and studied several derivatives of these sulphonic acids containing bromine, and have succeeded in establishing the constitution of these various products.

δ-*Sulphopyromucic Acid.*

If dry pyromucic acid is slowly added to fuming sulphuric acid (sp. gr. 1.95), it dissolves without serious discoloration, and in a short time the formation of the sulphonic acid is complete. We have usually taken three parts of sulphuric acid to one of pyromucic, and have allowed the viscous solution to stand for twenty-four hours before diluting and neutralising with baric carbonate. The aqueous solution filtered from the baric sulphate and concentrated by evaporation deposits on cooling globular aggregations of minute crystals which are readily purified by recrystallisation

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1886, by Arthur W. Palmer, then candidate for the degree of Doctor of Science.

[3] Ann. Chem. (Liebig), **116**, 268.

from hot water. The acid prepared by exact precipitation with sulphuric acid is extremely soluble in water, but may be obtained by concentration in large transparent prisms which deliquesce in moist air.

Baric δ-Sulphopyromucate, $BaC_5H_2SO_6.4H_2O$.—This salt crystallises in thin flat prisms which are usually closely aggregated in hemispherical masses. It is readily soluble in hot water, more sparingly soluble in cold water, and its aqueous solution is precipitated by the addition of alcohol. When dried by exposure to the air it contains four molecules of water, a part of which it slowly loses over sulphuric acid or at 100°, the rest at 160°.

I. 2.1205 grams of the air-dried salt lost, at 162°, 0.3827 gram H_2O.

II. 2.5754 grams of the air-dried salt lost, at 160°, 0.4605 gram H_2O.

	Calculated for $BaC_5H_2SO_6.4H_2O$.	Found. I.	Found. II.
H_2O	18.02	18.05	17.88

I. 0.7695 gram of the salt dried at 160° gave 0.5480 gram $BaSO_4$.

II. 0.7010 gram of the salt dried at 160° gave 0.4990 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found. I.	Found. II.
Ba	41.90	41.87	41.85

The solubility of the salt in cold water we have determined according to the method of V. Meyer.

I. 15.1350 grams of a solution saturated at 21° gave 0.3672 gram $BaSO_4$.

II. 13.9856 grams of a solution saturated at 21° gave 0.3384 gram $BaSO_4$.

The aqueous solution saturated at 21° therefore contained the following percentages of the anhydrous salt:

I.	II.
3.40	3.39

Acid Baric δ-Sulphopyromucate, $Ba(C_5H_2SO_6)_2.4H_2O$ and $6H_2O$.—Although this salt may be formed by the action of hydrochloric acid upon the neutral salt, its ready solubility in cold water makes it more conveniently prepared from equivalent quantities of the free acid and the neutral salt. On cooling the concentrated

solution, the salt separates in long slender prisms containing six molecules of water. From more dilute solutions, when crystallisation begins at ordinary temperatures, the salt separates in well formed rhombic plates which contain four molecules of water. Not unfrequently both forms appear together, and we have not been able to determine with precision the conditions essential to the formation of either. The long slender prisms effloresce slowly when exposed to the air. When dried by pressure and by short exposure to the air, it gave the following results:

I. 0.6298 gram of the salt lost, at 100°, 0.1056 gram H_2O.

II. 1.7845 gram of the salt lost, at 120°, 0.3055 gram H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2.6H_2O$.	Found. I.	II.
H_2O	17.22	16.77	17.12

I. 0.5242 gram of the salt dried at 100° gave 0.2361 gram $BaSO_4$.

II. 0.7035 gram of the salt dried at 120° gave 0.3155 gram $BaSO_4$.

III. 0.7629 gram of the salt dried at 120° gave 0.3420 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	Found. I.	II.	III.
Ba	26.39	26.48	26.36	26.35

The rhombic plates did not lose in weight when exposed to the air, and but slowly over sulphuric acid. The air-dried salt gave the following results:

I. 4.3735 grams of the air-dried salt lost, at 105°, 0.5235 gram H_2O.

II. 1.4496 gram of the air-dried salt lost, at 105°, 0.1762 gram H_2O.

III. 1.6332 gram of the air-dried salt lost, at 135°, 0.2010 gram H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2.4H_2O$.	I.	Found. II.	III.
H_2O	12.18	11.97	12.16	12.31

I. 0.6969 gram of the salt dried at 105° gave 0.3125 gram $BaSO_4$.

II. 0.6325 gram of the salt dried at 140° gave 0.2825 gram $BaSO_4$.

III. 0.5982 gram of the salt dried at 140° gave 0.2682 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	Found. I.	II.	III.
Ba	26.39	26.36	26.26	26.36

Calcic δ-Sulphopyromucate, $CaC_5H_2SO_6.3H_2O$.—This salt is quite soluble in cold water, and crystallises in flat concentrically grouped prisms which slowly effloresce over sulphuric acid.

0.7413 gram of the salt lost, at 130°, 0.1364 gram H_2O.

	Calculated for $CaC_5H_2SO_6.3H_2O$.	Found.
H_2O	19.01	18.40

I. 0.5737 gram of the salt dried at 125° gave 0.3383 gram $CaSO_4$.

II. 0.6405 gram of the salt dried at 125° gave 0.3770 gram $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	Found. I.	II.
Ca	17.40	17.34	17.31

Plumbic δ-Sulphopyromucate, $PbC_5H_2SO_6.2H_2O$.—This salt is readily soluble in hot water, more sparingly in cold, and crystallises in clustered needles. The air-dried salt contained two molecules of water.

2.1320 grams of the air-dried salt lost at 105° 0.1805 gram H_2O.

	Calculated for $PbC_5H_2SO_6.2H_2O$.	Found.
H_2O	8.31	8.47

I. 0.6682 gram of the salt dried at 110° gave 0.5085 gram $PbSO_4$.

II. 0.5046 gram of the salt dried at 110° gave 0.3837 gram $PbSO_4$.

III. 1.0150 gram of the salt dried at 110° gave 0.5570 gram CO_2 and 0.0660 gram H_2O.

	Calculated for $PbC_5H_2SO_6$.	Found. I.	II.	III.
Pb	52.14	51.99	51.96	
C	15.16	...	...	14.97
H	0.50	...	...	0.72

Argentic δ-Sulphopyromucate, $Ag_2C_5H_2SO_6$.—The silver salt is sparingly soluble in cold water, somewhat more readily soluble in hot water, and crystallises in short thick prisms. The air-dried salt lost slightly in weight when heated at 120°, but the loss was insignificant.

I. 0.6788 gram of the salt gave 0.4779 gram AgCl and 0.3923 gram $BaSO_4$.

II. 0.5255 gram of the salt gave 0.3703 gram AgCl and 0.3028 gram $BaSO_4$.

	Calculated for $Ag_2C_5H_2SO_4$.	Found. I.	II.
Ag	53.21	53.01	53.04
SO_3	19.97	19.85	19.78

Potassic δ-Sulphopyromucate, $K_2C_5H_2SO_4.4H_2O$.—The potassium salt is extremely soluble even in cold water, and crystallises in long slender prisms which apparently contain four molecules of water. They effloresce quite rapidly when exposed to the air, and our determinations of the water of crystallisation are, therefore, not entirely satisfactory.

I. 2.4108 grams of the salt dried by short exposure to the air lost, at 135°, 0.4966 gram H_2O.

II. 0.9701 gram of the salt dried by pressure only lost, at 100°, 0.2074 gram H_2O.

III. 1.3420 gram of the salt dried by short exposure to the air lost, at 115°, 0.2775 gram H_2O.

	Calculated for $K_2C_5H_2SO_4.4H_2O$.	Found. I.	II.	III.
H_2O	21.15	20.60	21.38	20.68

I. 0.5573 gram of the anhydrous salt gave 0.3608 gram K_2SO_4.

II. 0.5035 gram of the anhydrous salt gave 0.3242 gram K_2SO_4.

	Calculated for $K_2C_5H_2SO_4$.	Found. I.	II.
K	29.16	29.07	28.91

Acid Potassic δ-Sulphopyromucate, $KC_5H_2SO_4$.—The acid potassium salt is very soluble in water, and crystallises in large anhydrous prisms.

I. 0.8655 gram of the salt gave 0.3253 gram K_2SO_4.

II. 0.8290 gram of the salt gave 0.3127 gram K_2SO_4.

III. 0.7694 gram of the salt gave 0.2879 gram K_2SO_4.

	Calculated for $KC_5H_2SO_4$.	Found. I.	II.	III.
K	16.99	16.89	16.93	16.81

Sodic δ-Sulphopyromucate, $Na_2C_5H_2SO_4.5H_2O$.—The neutral sodium salt is extremely soluble in water, and crystallises in long slender needles which appear to contain five molecules of water.

The same salt is obtained in the form of fine felted needles by crystallisation from dilute alcohol.

I. 1.5082 gram of the salt dried by short exposure to the air lost, at 110°, 0.3970 gram H_2O.

II. 1.4198 gram of the salt recrystallised from dilute alcohol and dried by short exposure to the air lost, at 135°, 0.3773 gram H_2O.

III. 1.0232 gram of the salt recrystallised from dilute alcohol and dried by pressure only, lost, at 135°, 0.2785 gram H_2O.

	Calculated for $Na_2C_5H_2SO_6.5H_2O$.	Found. I.	II.	III.
H_2O	27.61	26.32	26.57	27.22

I. 0.5195 gram of the salt dried at 110° gave 0.3115 gram Na_2SO_4.

II. 0.5592 gram of the salt dried at 110° gave 0.3357 gram Na_2SO_4.

	Calculated for $Na_2C_5H_2SO_6$.	Found. I.	II.
Na	19.49	19.43	19.45

Acid Sodic δ-Sulphopyromucate, $NaC_5H_3SO_6.H_2O$.—This salt crystallises in long slender prisms which do not lose in weight when exposed to the air or over sulphuric acid.

I. 2.1303 grams of the air-dried salt lost, at 110°, 0.1658 gram H_2O.

	Calculated for $NaC_5H_3SO_6.H_2O$.	Found.
H_2O	7.76	7.78

I. 1.0224 gram of the salt dried at 110° gave 0.3371 gram Na_2SO_4.

II. 0.9498 gram of the salt dried at 110° gave 0.3154 gram Na_2SO_4.

	Calculated for $NaC_5H_3SO_6$.	Found. I.	II.
Na	10.75	10.69	10.76

δ-Sulphopyromucamide, $C_5H_3SO_4(NH_2)_2$.—By acting upon the dry sodium salt of δ-sulphopyromucic acid with phosphoric pentachloride, and expelling at a gentle heat the greater part of the phosphoric oxychloride formed in the reaction, a viscous oil was obtained which did not invite further investigation. It was, therefore, at once converted into the corresponding amide by the action of concentrated ammonic hydrate. The product of the reaction, after recrystallisation from boiling water, formed long flat prisms

readily soluble in hot water, sparingly soluble in cold water, which melted at 213°.

I. 0.3441 gram of substance gave 47.2 cc. moist nitrogen at 27° and under a pressure of 763 mm.

II. 0.2025 gram of substance gave 0.2507 gram $BaSO_4$.

	Calculated for $C_5H_2SO_4(NH_2)_2$.	Found. I.	II.
N	14.73	15.18	
S	16.84	...	17.00

Action of Bromine.

At ordinary temperatures dry bromine has little or no action upon dry δ-sulphopyromucic acid. At 100° in a sealed tube a complicated reaction ensues which we have not yet fully investigated. Ordinary dibromsuccinic acid is formed in considerable quantity, and at the same time a small amount of mucobromyl bromide, as was shown by the blue color developed in alkaline solution, and by the formation of mucobromic acid melting at 120°–121° on heating with water. There was also formed in small quantity a beautifully crystalline substance, sparingly soluble even in boiling alcohol, which contained sulphur but no bromine. This substance we unfortunately have not yet succeeded in obtaining in quantity sufficient for further study.

In aqueous solution bromine rapidly oxidises δ-sulphopyromucic acid, even in the cold. The final product of the reaction is fumaric acid, and we have hitherto been unable to isolate any intermediate products. It is probable, however, that maleic acid is in fact the first product of the oxidation. If bromine be added to an aqueous solution of the barium salt of the acid, baric sulphate is immediately thrown down; but since the amount of baric sulphate thus formed is slightly less than the theoretical quantity, secondary products containing sulphur are doubtless formed. In the complete oxidation of the acid we have used a slight excess of bromine, and have finished the reaction by gentle heat. The fumaric acid obtained was identified by qualitative tests and by the analysis of the silver salt.

I. 0.2124 gram of the salt dried at 120° gave 0.2406 gram AgBr.

II. 0.2056 gram of the salt dried at 120° gave 0.2332 gram AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found. I.	II.
Ag	65.46	65.07	65.15

The decomposition with bromine, therefore, takes place in great part according to the equation,

$$C_5H_4SO_6 + 3Br_2 + 4H_2O = C_4H_4O_4 + CO_2 + H_2SO_4 + 6HBr.$$

Action of Nitric Acid.

The oxidation of δ-sulphopyromucic acid with dilute nitric acid takes place but slowly, and even after long boiling with moderately concentrated acid the decomposition is far from complete. After boiling for some time with acid of sp. gr. 1.20 and evaporation upon the water-bath, fumaric acid was obtained, together with small quantities of oxalic acid. The fumaric acid was identified, as before, by its physical properties and by analysis of its silver salt.

0.1508 gram of the salt dried at 125° gave 0.1710 gram AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65 46	65.15

The reaction with concentrated nitric acid is much more interesting, since the sulpho group is in this way replaced by the nitro group and the δ-nitropyromucic acid of Klinkhardt,[1] formed with comparatively little oxidation. This replacement is slowly effected at ordinary temperatures, but rapidly at 100°. Dry sulphopyromucic acid is slowly added to several times its weight of cold fuming nitric acid. The mixture is at first cooled, and the reaction afterward completed by gentle heat. The nitric acid is then partially removed by evaporation, and the nitropyromucic acid, which separates as the solution cools, recrystallised from hot water. For its complete purification we found it necessary to dissolve the acid in a cold dilute solution of sodic carbonate, to extract with ether this alkaline solution, and to recrystallise from hot water the product obtained by the addition of hydrochloric acid. The pale yellow acid thus obtained crystallised in rectangular plates which melted at 182°–183°.

0.4925 gram substance gave 37.9 cc. of moist nitrogen at 16° and under a pressure of 748 mm.

	Calculated for $C_5H_3(NO)_3O_3$.	Found.
N	8.91	8.82

The ethyl ether of the acid was easily formed by warming its alcoholic solution with concentrated sulphuric acid. It was spar-

[1] J. prak. Chem. N. F. 23, 41.

ingly soluble in cold alcohol, and crystallised in broad lustrous plates which melted at 99°–100°. Klinkhardt gives the melting point of the acid as 183°, and of the ether as 101°.

With the δ-nitropyromucic acid is formed in small quantity a neutral substance containing nitrogen, which was obtained by evaporating the ether used in the extraction of the alkaline solution of the crude nitropyromucic acid. The same substance was formed in somewhat larger quantity when we attempted to prepare nitropyromucic acid without isolating the sulphonic acid by the addition of nitric acid to a solution of pyromucic acid in fuming sulphuric acid. The substance dissolved sparingly in boiling water, and crystallised on cooling in clustered prisms which melted at 100°–101°. On warming with sodic hydrate a bright yellow color was developed. A filter paper moistened with its alcoholic solution and exposed to the vapors of ammonic sulphide turned yellow at first, then salmon-red. This behavior corresponds closely with that observed by V. Meyer[1] and Otto Stadler in the case of nitro derivatives of thiophen. Although from lack of material we have as yet made no analyses of this substance, we shall describe later a dibromdinitrofurfuran,[2] which was obtained under similar conditions from the βγ-dibrom-δ-sulphopyromucic acid, whose formation leaves no doubt that this substance is in fact αα-dinitrofurfuran. It will be further studied in the future in this laboratory.

Fusing potassic hydrate converts the δ-sulphopyromucic acid into succinic acid, and at the same time more or less oxalic acid is formed. Although we have also made certain experiments concerning the action of fusing sodic formiate, we have as yet reached no satisfactory conclusion, and must therefore postpone all consideration of our results until we have made further investigations.

β-Brom-δ-Sulphopyromucic Acid.

Although we have not succeeded in preparing substitution products directly from δ-sulphopyromucic acid, they may readily be made by the action of fuming sulphuric acid upon substituted pyromucic acids. If β-brompyromucic acid is dissolved in three times its weight of fuming sulphuric acid (sp. gr. 1.95), no carbonisation takes place at ordinary temperatures, and from the diluted solution may be isolated by neutralisation with baric carbonate the barium

[1] Ber. d. chem. Ges. **17**, 2779. [2] Page 391.

salt of β-brom-δ-sulphopyromucic acid. The free acid is extremely soluble even in cold water, and crystallises in radiating needles which deliquesce rapidly in moist air.

Baric β-Brom-δ-Sulphopyromucate, $BaC_5HBrSO_6.4H_2O$.—This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises in flat clustered prisms. It is precipitated in the form of fine needles on the addition of alcohol to its aqueous solution. The air-dried salt contains four molecules of water, most of which it loses over sulphuric acid, the rest at 100°.

I. 1.9130 gram of the air-dried salt lost, at 100°, 0.2824 gram H_2O.

II. 1.1010 gram of the air-dried salt lost, at 170°, 0.1630 gram H_2O.

	Calculated for $BaC_5HBrSO_6.4H_2O$.	Found. I.	II.
H_2O	15.06	14.76	14.80

I. 0.3030 gram of the salt dried at 170° gave 0.1740 gram $BaSO_4$.

II. 0.3293 gram of the salt dried at 170° gave 0.1886 gram $BaSO_4$.

	Calculated for BaC_5HBrSO_6.	Found. I.	II.
Ba	33.75	33.76	33.67

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 27.6020 grams of the solution saturated at 21° gave 0.2300 gram $BaSO_4$.

II. 27.9011 grams of the solution saturated at 21° gave 0.2369 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
1.45	1.48

Calcic β-Brom-δ-Sulphopyromucate, $CaC_5HBrSO_6.6H_2O$.—The calcium salt proved to be extremely soluble even in cold water. The syrupy solution gradually solidified, with the separation of long radiating needles. The air-dried salt apparently contained six molecules of water, five of which it rapidly lost over sulphuric acid.

I. 1.2305 gram of the air-dried salt lost, at 135°, 0.3193 gram H_2O.

II. 0.4444 gram of the air-dried salt gave 0.1413 gram $CaSO_4$.

	Calculated for $CaC_5HBrSO_6.6H_2O$.	Found. I.	Found. II.
H_2O	25.90	25.95	...
Ca	9.59	...	9.35

0.9631 gram of the salt dried over sulphuric acid lost, at 135°, 0.0519 gram H_2O.

	Calculated for $CaC_5HBrSO_6.H_2O$.	Found.
H_2O	5.51	5.39

0.4608 gram of the salt dried at 135° gave 0.1973 gram $CaSO_4$.

	Calculated for CaC_5HBrSO_6.	Found.
Ca	12.94	12.60

Plumbic β-Brom-δ-Sulphopyromucate, $PbC_5HBrSO_6.4H_2O$.—The lead salt is freely soluble in hot water, more sparingly in cold water, and crystallises in flat clustered prisms, or on rapid cooling in clustered needles. The air-dried salt contains four molecules of water, almost the whole of which it rapidly loses over sulphuric acid.

I. 1.3814 gram of the air-dried salt lost, at 130°, 0.1758 gram H_2O.

II. 1.9209 gram of the air-dried salt lost, at 140°, 0.2507 gram H_2O.

III. 0.3442 gram of the air-dried salt gave 0.1905 gram $PbSO_4$.

IV. 0.6382 gram of the air-dried salt gave 0.3530 gram $PbSO_4$.

	Calculated for $PbC_5HBrSO_6.4H_2O$.	Found. I.	II.	III.	IV.
H_2O	13.14	12.73	13.05	...	...
Pb	37.78	...	...	37.80	37.79

Potassic β-Brom-δ-Sulphopyromucate, $K_2C_5HBrSO_6.1\frac{1}{2}H_2O$ (?).—This salt is readily soluble in cold water, more sparingly soluble in dilute alcohol. It crystallises in small six-sided plates which are permanent in the air, but which effloresce over sulphuric acid. Two determinations of the water of crystallisation made in different preparations agree precisely with each other, but do not correspond well with any simple formula for the salt.

I. 0.8184 gram of the air-dried salt lost, at 160°, 0.0537 gram H_2O.

II. 1.4398 gram of the air-dried salt lost, at 160°, 0.0942 gram H_2O.

	Calculated for $K_2C_5HBrSO_6.H_2O$.	Calculated for $K_2C_5HBrSO_6.1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	4.93	7.22	6.56	6.55

0.3652 gram of the salt dried at 160° gave 0.1825 gram K_2SO_4.

	Calculated for $K_2C_5HBrSO_6$.	Found.
K	22.52	22.44

The connection between this brom-sulphopyromucic acid and the ∂-sulphopyromucic acid could evidently be proved most neatly and directly by eliminating from it the bromine and examining carefully the sulphonic acid thus formed. By warming a strongly ammoniacal solution of the barium salt with zinc dust the bromine was quickly removed. The filtered solution was boiled with a slight excess of baric hydrate until all the ammonia was expelled and the zinc precipitated. The solution was then freed from the excess of baric hydrate by means of carbonic dioxide, and concentrated on the water-bath. On cooling, the solution deposited globular aggregations of colorless crystals which appeared to be identical with those of baric ∂-sulphopyromucate. The identity was fully established by analyses of the salt, and by determinations of its solubility in water.

I. 1.5700 gram of the air-dried salt lost, at 165°, 0.2803 gram H_2O.

II. 0.7309 gram of the air-dried salt gave 0.4295 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6.4H_2O$.	Found. I.	II.
H_2O	18.02	17.85	...
Ba	34.34	...	34.55

0.4947 gram of the salt dried at 165° gave 0.3505 gram $BaSO_4$

	Calculated for $BaC_5H_2SO_6$.	Found.
Ba	41.90	41.67

I. 12.0595 grams of the solution saturated at 21° gave 0.2985 gram $BaSO_4$.

II. 12.1863 grams of the solution saturated at 21° gave 0.2989 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
3.47	3.44

These results are sufficient to prove that the sulphonic acid formed by the reduction of the β-brom-δ-sulphopyromucic acid is identical with that obtained directly from pyromucic acid by the action of sulphuric acid.

Action of Bromine.

Bromine in aqueous solution readily oxidises β-brom-δ-sulphopyromucic acid or its salts. Since the relative position of the bromine and the sulpho group had already been established, we thought it necessary to do no more than identify the final product of the oxidation. Bromine was added in slight excess to an aqueous solution of the barium salt, and the reaction completed at a gentle heat. The strongly acid solution was filtered from the baric sulphate which had been formed, and extracted with ether. The ether left on evaporation a white crystalline acid which softened somewhat at 120° and melted completely at 165°. After two recrystallisations from water the acid melted sharply at 176°–177°, and was therefore monobromfumaric acid. The oxidation took place according to the following equation:

$$C_5H_3BrSO_6 + 3Br_2 + 4H_2O = C_4H_3BrO_4 + CO_2 + H_2SO_4 + 6HBr.$$

Action of Nitric Acid.

We have made no experiments concerning the action of dilute nitric acid upon β-brom-δ-sulphopyromucic acid, since it could safely be assumed that oxidation would ensue as with the δ-sulphopyromucic acid, and that monobromfumaric acid would be formed. It seemed to us, however, of decided interest to act upon the acid with fuming nitric acid, since a bromnitropyromucic acid should then result. Dry β-brom-δ-sulphopyromucic acid was slowly added to three times its weight of fuming nitric acid. The reaction progressed slowly in the cold, more rapidly on warming, and without any considerable oxidation. After the reaction was completed, the greater part of the nitric acid was expelled by gentle heat, the crystalline acid left was dissolved in a dilute solution of sodic carbonate, and the alkaline solution then extracted with ether. Upon evaporation of the ether a small quantity of a neutral oil was left, which gradually solidified. The quantity of the product which we thus obtained was so minute that further investigation was out of the question. The alkaline solution when acidified and again extracted with ether yielded in abundance a crystalline acid which

proved to be β-brom-δ-nitropyromucic acid. It was readily soluble in alcohol, ether, or hot benzol, more sparingly in cold benzol. It dissolved freely in hot water, and as the solution cooled it was deposited in long clustered flattened needles which contained one molecule of water. The anhydrous acid melted at 159°–160°. At 100° the acid appeared to sublime slowly.

I. 1.2492 gram of the acid crystallised from water lost, at 60°, 0.0911 gram H_2O.[1]

II. 0.9980 gram of the acid crystallised from water lost, at 78°, 0.0740 gram H_2O.

	Calculated for $C_5H_2Br(NO_2)O_3.H_2O$.	Found. I.	II.
H_2O	7.09	7.29	7.42

I. 0.2065 gram of the acid dried at 100° gave 0.1652 gram AgBr.

II. 0.2648 gram of the acid dried at 100° gave 14.2 cc. of moist nitrogen at 20° and under a pressure of 763 mm.

	Calculated for $C_5H_2Br(NO_2)O_3$.	Found. I.	II.
Br	33.90	34.04	...
N	5.93	...	6.15

This acid will be further studied in this laboratory. There can be no doubt, however, that, like the nitropyromucic acid of Klinkhardt, it contains the nitro group in the δ position.

$\beta\gamma$-Dibrom-δ-Sulphopyromucic Acid.

$\beta\gamma$-dibrompyromucic acid dissolves in fuming sulphuric acid without the slightest carbonisation, and is converted in a short time into the corresponding sulphonic acid. A large part of our work was done with material made from pure $\beta\gamma$-dibrompyromucic acid. We subsequently found, however, as will be described more at length later in this paper, that the $\beta\delta$-dibrompyromucic was but little affected by fuming sulphuric acid if the action were not too long continued, and that the mixture of the isomeric dibrompyromucic acids obtained from pyromucic tetrabromide could therefore advantageously be employed direct. The mixed acids were dissolved in once and a half their weight of fuming sulphuric acid, and the solution diluted with water after the lapse of two or three hours. The $\beta\delta$-dibrompyromucic acid thus precipitated was removed by filtration, and the solution neutralised as usual by

[1] A slight mechanical loss renders the result of this determination uncertain in the second decimal place.

baric carbonate. The small amount of $\beta\delta$-dibrompyromucic acid, or its decomposition products, which remained in solution, could readily be removed by the recrystallisation of the barium salt which was obtained after evaporation. Since the separation of the isomeric dibrompyromucic acids is a matter of some difficulty, the preparation of the sulphonic acid in question is thus greatly facilitated. The free acid is very soluble even in cold water, but is more sparingly soluble in ordinary concentrated sulphuric acid. From sulphuric acid it crystallises in clustered needles, from water it is deposited in broad flat prisms which are permanent under ordinary atmospheric conditions.

Baric $\beta\gamma$-Dibrom-δ-Sulphopyromucate, $BaC_5Br_2SO_6.5H_2O$.—This salt is very readily soluble in hot water, more sparingly in cold water. The hot saturated solution solidifies on cooling, with the separation of long silky radiating needles. The air-dried salt contains five molecules of water, a part of which it loses over sulphuric acid.

I. 1.5136 gram of the air-dried salt lost, at 125°, 0.2422 gram H_2O.

II. 1.7684 gram of the air-dried salt lost, at 160°, 0.2855 gram H_2O.

III. 2.5118 grams of the air-dried salt lost, at 180°, 0.4013 gram H_2O.

	Calculated for $BaC_5Br_2SO_6.5H_2O$.	Found. I.	II.	III.
H_2O	15.65	16.01	16.14	15.97

I. 0.5378 gram of the salt dried at 125° gave 0.2575 gram $BaSO_4$.

II. 0.4688 gram of the salt dried at 180° gave 0.2243 gram $BaSO_4$.

III. 0.5317 gram of the salt dried at 180° gave 0.2550 gram $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6$.	Found. I.	II.	III.
Ba	28.25	28.15	28.13	28.19

The solubility of the salt in cold water we determined in the usual way.

I. 10.9011 grams of the solution saturated at 20° gave 0.2170 gram $BaSO_4$.

II. 11.9609 grams of the solution saturated at 20° gave 0.2398 gram $BaSO_4$.

The solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
4.14	4.17

When an aqueous solution of the barium salt is evaporated at 100°, small clear prisms separate, which contain less water than the salt just described. We found it impossible to prepare this salt satisfactorily for analysis, since it at once took up water in the cold. A preparation which was removed from the hot solution and immediately dried by pressure with filter paper gave on analysis the following results:

I. 1.6161 gram of the salt lost, at 140°, 0.1767 gram H_2O.

II. 0.6265 gram of the salt gave 0.2665 gram $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6.3H_2O$.	Found. I.	II.
H_2O	10.02	10.93	...
Ba	25.42	...	25.01

Plumbic βγ-Dibrom-δ-Sulphopyromucate, $PbC_5Br_2SO_6.4H_2O$.—The lead salt is readily soluble in hot water, more sparingly in cold, and crystallises in fine felted needles which are permanent in the air, but effloresce over sulphuric acid.

I. 1.4993 gram of the air-dried salt lost, at 165°, 0.1686 gram H_2O.

II. 1.0386 gram of the air-dried salt lost, at 165°, 0.1159 gram H_2O.

III. 0.6246 gram of the air-dried salt gave 0.3015 gram $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6.4H_2O$.	Found. I.	II.	III.
H_2O	11.48	11.24	11.16	...
Pb	33.01	...	...	32.98

0.5019 gram of the salt dried at 165° gave 0.2741 gram $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6$.	Found.
Pb	37.32	37.32

Argentic βγ-Dibrom-δ-Sulphopyromucate, $Ag_2C_5Br_2SO_6.H_2O$.—The silver salt is sparingly soluble in cold water, more readily in hot, and crystallises in large rhombic plates.

1.0216 gram of the air-dried salt lost, at 120°, 0.0339 gram H_2O.

	Calculated for $Ag_2C_5Br_2SO_6.H_2O$.	Found.
H_2O	3.09	3.31

I. 0.3016 gram of the salt dried at 120° gave 0.1520 gram AgCl.
II. 0.3021 gram of the salt dried at 120° gave 0.1522 gram AgCl.

	Calculated for $Ag_2C_4Br_2SO_5$.	Found. I.	II.
Ag	38.30	37.93	37.93

Potassic βγ-Dibrom-δ-Sulphopyromucate, $K_2C_5Br_2SO_6.H_2O$.—The potassium salt is readily soluble in hot water, more sparingly soluble in cold water. It crystallises in flat, obliquely truncated prisms.

I. 1.0634 gram of the air-dried salt lost, at 135°, 0.0377 gram H_2O.

II. 0.5307 gram of the air-dried salt gave 0.2072 gram K_2SO_4.

	Calculated for $K_2C_5Br_2SO_6.H_2O$.	Found. I.	II.
H_2O	4.05	3.55	...
K	17.60	...	17.53

0.4507 gram of the salt dried at 135° gave 0.1823 gram K_2SO_4.

	Calculated for $K_2C_5Br_2SO_6$.	Found.
K	18.35	18.16

From the structure of the βγ-dibrompyromucic acid, which has already been determined by Hill and Sanger,[1] it is evident that a sulphonic acid formed from it must of necessity contain the sulpho group in the δ position. It therefore seemed to us of interest to prepare from this βγ-dibrom-δ-sulphopyromucic acid, by the elimination of the bromine, the corresponding sulphopyromucic acid. Should this acid prove to be identical with that made directly from pyromucic acid by means of sulphuric acid, the δ position of the sulpho group in the latter acid would be established with precision. A strongly ammoniacal solution of baric βγ-dibrom-δ-sulphopyromucate was warmed for some time with an excess of zinc dust. After reduction had taken place the filtered solution was boiled with an excess of baric hydrate until the ammonia had been expelled, and the excess of baric hydrate then removed with carbonic dioxide. The concentrated solution deposited on cooling hemispherical aggregations of colorless crystals, which upon investigation proved to be identical in composition with the baric sulphopyromucate already described, and to have also the same solubility in cold water.

0.6194 gram of the air-dried salt lost, at 160°, 0.1111 gram H_2O, and gave 0.3614 gram $BaSO_4$.

[1] Proceedings Amer. Acad. **21**, 181.

	Calculated for $BaC_5H_2SO_6.4H_2O$.	Found.
H_2O	18·02	17·94
Ba	34·34	34·30

I. 12.9988 grams of the solution saturated at 21° gave 0.3169 gram $BaSO_4$.

II. 13.0993 grams of the solution saturated at 21° gave 0.3181 gram $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
3·42	3·41

It will be seen that these results prove the identity of this salt with that made directly from pyromucic acid.

Action of Bromine.

Bromine in aqueous solution readily oxidises $\beta\gamma$-dibrom-δ-sulphopyromucic acid or its salts. If a slight excess of bromine is added to an aqueous solution of the barium salt, baric sulphate is at once precipitated, and after the reaction is completed by gentle heat, ether extracts from the filtered solution dibrommaleic acid. The anhydride formed by sublimation was found to melt at the proper point, 114°–115°.

Action of Nitric Acid.

Diluted nitric acid oxidises $\beta\gamma$-dibrom-δ-sulphopyromucic acid on heating and forms dibrommaleic acid, whose identity we established through the melting point of its anhydride, 114°–115°. By the action of fuming nitric acid a nitro acid is formed. The dry acid was slowly added to several times its weight of fuming nitric acid. At first the mixture was cooled, afterwards warmed, and the greater part of the nitric acid then expelled by gentle heat. The crystalline product of the reaction was in part an acid quite readily soluble in hot water, and in part a neutral substance which dissolved with more difficulty in boiling water. For the complete separation of these two substances we treated the product with a dilute solution of sodic carbonate and extracted with ether. The alkaline solution was then acidified and the acid extracted with ether. After several recrystallisations from hot water it formed finely felted yellow needles, which were sparingly soluble in cold water, more readily in hot, and melted at 204°–205°. They dissolved freely in

alcohol, ether, or in benzol. Analysis showed the substance to be a dibromnitropyromucic acid.

I. 0.1050 gram of the acid gave 0.1260 gram AgBr.

II. 0.2970 gram of the acid gave 11.7 cc. of moist nitrogen at 21° under a pressure of 758 mm.

	Calculated for $C_5HBr_2(NO_2)O_3$.	Found.
Br	50.79	51.07
N	4.44	4.47

The mode of its formation shows that this acid must of necessity be the $\beta\gamma$-dibrom-δ-nitropyromucic acid.

The ether which had been used for extracting the alkaline solution of the crude nitro product left, on evaporation, a quantity of a yellow crystalline solid which was sufficient to enable us to establish its identity by analysis. The substance was sparingly soluble even in hot water, and crystallised on slow cooling in stout prisms, or on rapid cooling and scratching in felted needles. In alcohol it was sparingly soluble; but benzol dissolved it freely, and on standing the solution deposited quite large transparent yellow prisms which effloresced rapidly on exposure to the air. The melting point to the effloresced substance was 150°–151°, and the percentage of bromine it contained showed that it was a dibromdinitrofurfuran.

0.2008 gram of the substance gave 0.2396 gram AgBr.

	Calculated for $C_4Br_2(NO_2)_2O$.	Found.
Br	50.63	50.79

The clear crystals deposited from benzol evidently contained benzol of crystallisation. They effloresced so rapidly, however, that the exact determination of the combined benzol was somewhat difficult.

0.2611 gram of the substance rapidly pressed and weighed lost, on standing exposed to the air until the weight was constant, 0.0486 gram benzol.

	Calculated for $C_4Br_2(NO_2)_2O.C_6H_6$.	Found.
C_6H_6	19.80	18.61

Considering the difficulty of such determinations, this result leaves no doubt that this dibromdinitrofurfuran crystallises with one molecule of benzol. The mode of formation of this substance leaves no possible doubt that it is the $\alpha\alpha$-dinitro-$\beta\beta$-dibromfurfuran.

(To be concluded.)

ON THE DENSITIES AND REFRACTIVE INDICES OF CERTAIN OILS.

By J. H. Long.

In the course of a somewhat extended investigation on fats and oils I found it desirable to make full determinations of specific gravity and index of refraction.

For some oils these data are not to be found in the literature, and in most cases where given they are more or less incomplete. In the following pages I present the results obtained with oils of known purity, and will describe first the method of experiment.

Specific Gravity.

This was found by means of a 50 gram pycnometer with capillary stopper, and was determined at four temperatures obtained by immersion in water in the usual manner. A large volume of water was employed and its temperature kept constant, as shown by an accurately corrected thermometer. The temperature of the oil in the vessel was known to a tenth of one degree C. The volume and cubic expansion of the pycnometer were determined by special experiments. In the final reductions all weights were calculated to the value in vacuo, and the specific gravities referred to water at 4° C. as unity.

The Index of Refraction.

For these determinations I employed the method of minimum deviation, making use of an excellent Meyerstein spectrometer and hollow prism from which readings to 30″ could be obtained. The refractive index is given by the formula $N = \frac{\sin \frac{A+d}{2}}{\sin \frac{A}{2}}$ in which A is the refractive angle of the prism and d the observed angle of minimum deviation. Some of the experiments were carried out in a cold room in winter, while others were performed in the summer. To determine the refraction at higher temperatures, the prism, resting on its brass table, was placed on a warm iron plate, and allowed to remain there until a thermometer inserted in the top opening of the prism showed the required

elevation. The prism and table were then returned to the instrument, their position was adjusted by means of leveling screws and the readings commenced. (The arrangement of the apparatus is shown in Wüllner's Lehrbuch der experimental Physik, II, 129). By making duplicate experiments, and taking the mean values, results accurate to four decimal places of N are obtained. In the following tables the corrected temperature readings are given, the thermometer used being the same as that employed in the determination of density. As source of light I used the sodium flame obtained by fusing a bead of sodium carbonate over a Bunsen burner.

Olive Oil.

We find various statements in the books regarding the density of pure olive oil. For a temperature of 15° C. the values vary from .9120 to .9250, or even higher. Many chemists claim that these limits are too wide for pure oils, but it must be remembered that the products are extracted and refined by quite different processes. The hot pressed oils contain considerable palmitin, solidify, therefore, sooner, and show a higher density. Out of a number of samples examined I can report on four of known purity. One of these samples was pressed in Southern California from native olives; the others were pressed in France. Not one of these samples deposited palmitin above 0° C. Although thick, they remained perfectly clear, which suggests to me that the statements usually found in the books regarding the temperature of solidification of olive oil must have been derived from a study of inferior or warm pressed oils rich in palmitin. Allen, however, gives the solidifying point as $+4$ to $-6°$ C.

The specific gravity (D) and the refractive index (N) of these oils I found as follows:

No. 1. Pressed in France.

T.	D.	T.	N.
3.5°	.9240	14.5°	1.4716
19.5	.9131	20.5	1.4693
36.0	.9022	23.5	1.4681
45.9	.8955	26.6	1.4673
		30.7	1.4657
		35.9	1.4637
		41.1	1.4620

No. 5. Pressed in California.

T.	D.	T.	N.
4.5°	.9240	16.3°	1.4712
18.0	.9149	19.3	1.4700
31.1	.9062	23.4	1.4684
49.7	.8938	25.4	1.4677
		29.3	1.4663
		34.3	1.4643
		39.3	1.4622

No. 10. Pressed in France.

T.	D.	T.	N.
2.6°	.9252	15.8°	1.4731
19.5	.9132	20.3	1.4708
33.5	.9039	23.3	1.4694
49.4	.8935	24.8	1.4687
		26.8	1.4679
		30.8	1.4663
		42.2	1.4626

No. 11. Pressed in France.

T.	D.	T.	N.
4.4°	.9238	14.8°	1.4734
19.8	.9128	17.3	1.4722
32.5	.9044	19.3	1.4714
50.6	.8924	21.8	1.4703
		24.3	1.4693
		27.8	1.4677
		30.8	1.4665
		34.3	1.4651

The variation in the specific gravity seems to be the same for all samples, and amounts to about .00066 for each degree. Schaedler (Technologie der Fette und Oele u. s. w.) gives almost the same coefficient for pure samples, and .9177 as the specific gravity at 15° C. Allen gives .914 to .917 as the probable variations. Quincke (Ber. Acad. Ber. 1883, 409) gives 1.4690 as the value of the refractive index at 20.5° C.

This is close to the values found for Nos. 1 and 5, but somewhat lower than those found for Nos. 10 and 11.

The temperature variation of N amounts to nearly .0004 for each degree between 20° and 35°.

Cottonseed Oil.

Because of the great practical importance and increasing consumption of this article, I have made numerous tests of samples obtained from different sources. In the last few years great improvements have been made in the processes of refining cottonseed oil, in consequence of which much of the product now on the market does not correspond to the tests usually given. Cottonseed oil can be refined (and practically is) until it is as clear and light as water. Such an oil contains few of the coloring or readily oxidisable matters which give the so-called *color* or *heat* reactions so often employed. The cold test (solidifying point) of such oils is likewise very much altered, and their detection when mixed with other oils made more difficult.

I have obtained the following results by direct experiment.

No. 7. A crude oil obtained in Chicago from a leading refiner. It deposits a sediment quickly when cooled below 15° C.

T.	D.	T.	N.
3.0°	.9325	27.9°	1.4694
16.6	.9233	35.3	1.4668
32.4	.9126	46.2	1.4624
46.5	.9030		

The specific gravity determination at the lowest temperature is probably somewhat inaccurate.

No. 8. A light yellow oil refined from No. 7. Remains clear at lowest temperature.

T.	D.	T.	N.
4.5°	.9291	19.3°	1.4744
18.2	.9198	22.8	1.4730
30.9	.9112	24.8	1.4722
45.4	.9014	28.3	1.4708
		36.3	1.4675
		44.2	1.4658

No. 9. A sample refined from No. 8. This is white and clear and bears no resemblance to ordinary cottonseed oils.

T.	D.	T.	N.
2.0°	.9312	18.3°	1.4736
17.9	.9202	22.3	1.4720
34.3	.9090	27.3	1.4700
47.0	.9006	31.3	1.4684
		35.3	1.4669
		40.2	1.4650

No. 12. A crude oil, very dark, but deposits a comparatively small sediment on cooling to 15° C. and below.

The sample is too dark for accurate determinations of the refractive index.

T.	D.	T.	N.
4.8°	.9290	21.0°	1.4708
18.6	.9199	23.0	1.4700
32.5	.9107		
49.6	.8994		

No. 6. A sample refined from the above in the laboratory, by partial saponification with a 1 per cent. solution of sodium carbonate, washing, and drying by means of a current of hot air. The product is yellow but perfectly clear.

T.	D.	T.	N.
3.8°	.9295	13.8°	1.4755
19.2	.9191	19.3	1.4730
31.4	.9108	23.3	1.4712
47.4	.9000	26.3	1.4703
		32.3	1.4681
		36.2	1.4667
		39.2	1.4660

No. 16. A clear yellow sample refined in New York.

T.	D.	T.	N.
0.7°	.9322	19.3°	1.4742
15.6	.9219	22.8	1.4728
30.5	.9117	25.3	1.4718
46.5	.9013	27.8	1.4708
		29.8	1.4700
		33.3	1.4686
		36.8	1.4672

The figures given above show that the temperature variations of specific gravity and refractive index are not very different from those of olive oil. The decrease in specific gravity at mean temperatures varies in the different samples between .00066 and .00068, while the variations in the refractive index are something less than .0004 for each degree.

The values found for the specific gravity of the crude samples are lower than those usually given, as will appear below.

Sesamé Oil.

Although this oil is made in large quantities in Europe, it is difficult to secure specimens here of guaranteed purity.

No. 4. A sample received from a Chicago importer.

T.	D.	T.	N.
3.3°	.9308	17.9°	1.4744
16.5	.9218	20.4	1.4733
32.4	.9111	24.4	1.4718
48.8	.9001	29.4	1.4698
		32.4	1.4687
		36.4	1.4672
		39.3	1.4661

No. 14. A sample refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

T.	D.	T.	N.
1.5°	.9326	14.3°	1.4771
18.5	.9209	18.3	1.4755
33.2	.9110	22.8	1.4736
47.4	.9016	24.8	1.4728
		26.8	1.4720
		30.3	1.4705
		34.3	1.4691
		39.2	1.4673

No. 18. A sample received from a New York importer.

T.	D.	T.	N.
5.5°	.9282	14.3°	1.4759
18.4	.9192	19.3	1.4739
34.6	.9081	20.3	1.4736
46.6	.8998	23.3	1.4724
		26.8	1.4710
		30.3	1.4694
		34.3	1.4678
		38.0	1.4664

The temperature changes are nearly identical with those given for olive and cottonseed oil, varying for the density between .00067 and .00069 for each degree.

Mustard Oil.

The oil of black mustard may be classed among the cheaper oils, and when properly refined has numerous uses. I have

examined two samples of known purity, and a third prepared from one of these by partial saponification. The first two had been well refined and were almost entirely free from the odor of the volatile oil.

No. 2. A sample obtained in Chicago.

T.	D.	T.	N.
4.0°	.9222	14.5°	1.4769
19.1	.9122	17.5	1.4751
34.0	.9026	20.5	1.4739
48.6	.8932	22.5	1.4732
		24.5	1.4724
		28.9	1.4706
		35.0	1.4683
		40.0	1.4663

No. 15. Oil refined from the above by treatment with a 1 per cent. solution of potassium hydrate.

T.	D.	T.	N.
1.5°	.9251	14.8°	1.4771
16.6	.9149	19.3	1.4749
33.6	.9037	21.3	1.4739
47.4	.8946	23.3	1.4729
		25.8	1.4720
		31.3	1.4700
		34.3	1.4688
		37.3	1.4677

No. 17. A sample obtained from a New York importer.

T.	D.	T.	N.
1.7°	.9239	15.3°	1.4759
18.6	.9128	19.3	1 4743
36.0	.9014	21.3	1.4736
45.8	.8948	23.8	1.4726
		27.3	1.4712
		31.8	1.4694
		36.8	1.4674
		39.3	1.4665

The temperature coefficients are nearly as observed in the other oils.

Peanut Oil.

One sample of oil, partiaily refined, was examined, with these results.

No. 19.

T.	D.	T.	N.
3.2°	.9309	15.8°	1.4736
17.9	.9186	19.8	1.4718
34.4	.9074	23.3	1.4704
47.7	.8984	25.3	1.4696
		28.3	1.4684
		34.3	1.4661
		39.2	1.4641

While the change in the density is comparatively rapid between the lowest temperatures, it amounts to .00068 for each degree between the mean temperatures, that is, the rate is about as before given. The variation in the refractive index is normal.

Castor Oil.

The following results were obtained by examination of a sample of well refined cold pressed oil.

No. 3.

T.	D.	T.	N.
4.0°	.9695	14.4°	1.4831
7.1	.9675	18.4	1.4806
18.0	.9602	20.4	1.4790
32.5	.9505	22.9	1.4781
46.8	.9410	25.4	1.4771
		28.4	1.4759
		33.9	1.4741
		37.3	1.4728

Lard Oil.

A sample of pure oil, pressed in Chicago, was examined and gave these figures. As it became thick at the lowest temperature, the density determination at that point is probably not quite accurate.

No. 13.

T.	D.	T.	N.
1.8°	.9287	20.3°	1.4685
15.5	.9154	24.3	1.4669
32.5	.9036	27.3	1.4657
48.5	.8926	29.3	1.4649
		32.3	1.4637
		36.3	1.4622
		39.2	1.4612

In order to compare the values for the different oils with each other as well as with similar data obtained by other observers, I have calculated from the above direct observations the numbers in the tables below. In most cases the curve representing the variations in specific gravity is nearly a straight line, and without introducing appreciable error it can be taken as linear between the intermediate temperatures. Assuming these points as correctly determined, I have interpolated values from 18° to 25° and for 30° and 35°.

By means of carefully drawn curves I have interpolated, from the direct determinations of N, the values for the same degrees of temperature. The numbers thus obtained are undoubtedly as accurate and satisfactory as could be obtained by a laborious method of calculation. Finally, I have calculated the "specific refractive energy," $\frac{N-1}{D}$, and give these values in another column.

Olive Oil, I.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9141	1.4702	.5144
19	.9134	1.4698	.5143
20	.9127	1.4695	.5143
21	.9121	1.4691	.5143
22	.9114	1.4688	.5144
23	.9107	1.4684	.5143
24	.9101	1.4680	.5142
25	.9094	1.4677	.5143
30	.9061	1.4658	.5142
35	.9028	1.4640	.5140

Olive Oil, II.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9139	1.4719	.5164
19	.9133	1.4715	.5163
20	.9126	1.4711	.5162
21	.9119	1.4707	.5162
22	.9112	1.4703	.5161
23	.9106	1.4698	.5159
24	.9099	1.4694	.5159
25	.9093	1.4690	.5158
30	.9060	1.4669	.5153
35	.9027	1.4648	.5148

Olive Oil, 10.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9142	1.4718	.5161
19	.9135	1.4714	.5160
20	.9129	1.4709	.5158
21	.9122	1.4705	.5158
22	.9115	1.4701	.5157
23	.9109	1.4696	.5155
24	.9102	1.4692	.5155
25	.9095	1.4688	.5154
30	.9062	1.4666	.5149
35	.9029	1.4645	.5148

Olive Oil, 5.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9149	1.4704	.5142
19	.9142	1.4701	.5142
20	.9136	1.4697	.5141
21	.9129	1.4693	.5141
22	.9122	1.4690	.5141
23	.9116	1.4685	.5140
24	.9109	1.4682	.5140
25	.9103	1.4678	.5139
30	.9069	1.4659	.5137
35	.9036	1.4640	.5135

Cottonseed Oil, 6.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9199	1.4735	.5147
19	.9192	1.4731	.5147
20	.9186	1.4727	.5146
21	.9179	1.4724	.5147
22	.9172	1.4720	.5147
23	.9165	1.4716	.5146
24	.9158	1.4712	.5145
25	.9151	1.4709	.5147
30	.9118	1.4690	.5144
35	.9084	1.4671	.5142

Cottonseed Oil, 7.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9224	1.4729	.5127
19	.9217	1.4725	.5127
20	.9210	1.4722	.5127
21	.9203	1.4718	.5127
22	.9196	1.4715	.5127
23	.9190	1.4711	.5126
24	.9183	1.4708	.5127
25	.9176	1.4704	.5127
30	.9142	1.4687	.5127
35	.9109	1.4670	.5127

Cottonseed Oil, 12.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9203		
19	.9196		
20	.9190		
21	.9183	1.4708	.5127
22	.9176		
23	.9170	1.4700	.5125
24	.9163		
25	.9157		
30	.9124		
35	.9090		

Cottonseed Oil, 8.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9199	1.4749	.5163
19	.9193	1.4745	.5162
20	.9186	1.4741	.5161
21	.9179	1.4737	.5161
22	.9172	1.4733	.5160
23	.9165	1.4729	.5160
24	.9159	1.4725	.5159
25	.9151	1.4721	.5159
30	.9118	1.4700	.5155
35	.9084	1.4680	.5152

Cottonseed Oil, 9.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9201	1.4737	.5148
19	.9194	1.4733	.5148
20	.9188	1.4730	.5148
21	.9180	1.4726	.5148
22	.9174	1.4722	.5147
23	.9167	1.4718	.5147
24	.9160	1.4714	.5146
25	.9154	1.4710	.5145
30	.9119	1.4690	.5143
35	.9085	1.4671	.5141

Sesamé Oil, 4.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9208	1.4742	.5150
19	.9201	1.4738	.5149
20	.9194	1.4735	.5150
21	.9188	1.4731	.5149
22	.9181	1.4727	.5149
23	.9174	1.4723	.5148
24	.9167	1.4719	.5148
25	.9161	1.4715	.5147
30	.9127	1.4696	.5145
35	.9093	1.4677	.5144

Cottonseed Oil, 16.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9203	1.4747	.5158
19	.9196	1.4743	.5158
20	.9189	1.4739	.5157
21	.9182	1.4735	.5157
22	.9176	1.4731	.5156
23	.9168	1.4727	.5156
24	.9162	1.4723	.5155
25	.9155	1.4719	.5155
30	.9120	1.4699	.5153
35	.9086	1.4679	.5150

Sesamé Oil, 14.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9212	1.4756	.5163
19	.9206	1.4752	.5162
20	.9199	1.4748	.5161
21	.9192	1.4744	.5161
22	.9185	1.4740	.5161
23	.9179	1.4736	.5160
24	.9172	1.4732	.5159
25	.9165	1.4728	.5159
30	.9132	1.4708	.5156
35	.9098	1.4688	.5153

Sesamé Oil, 18.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9195	1.4744	.5159
19	.9188	1.4740	.5159
20	.9181	1.4736	.5158
21	.9174	1.4732	.5158
22	.9167	1.4728	.5158
23	.9160	1.4724	.5157
24	.9154	1.4720	.5157
25	.9147	1.4716	.5156
30	.9113	1.4695	.5152
35	.9078	1.4675	.5150

Mustard Oil, 15.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9140	1.4754	.5201
19	.9133	1.4750	.5201
20	.9127	1.4746	.5200
21	.9120	1.4742	.5200
22	.9113	1.4738	.5199
23	.9107	1.4733	.5197
24	.9100	1.4730	.5198
25	.9094	1.4726	.5197
30	.9060	1.4705	.5193
35	.9028	1.4685	.5189

Mustard Oil, 2.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9129	1.4749	.5203
19	.9123	1.4745	.5201
20	.9116	1.4741	.5201
21	.9109	1.4737	.5199
22	.9103	1.4733	.5199
23	.9097	1.4729	.5198
24	.9090	1.4725	.5198
25	.9084	1.4722	.5198
30	.9052	1.4702	.5194
35	.9020	1.4683	.5192

Mustard Oil, 17.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9132	1.4748	.5199
19	.9125	1.4744	.5199
20	.9119	1.4740	.5198
21	.9112	1.4736	.5198
22	.9106	1.4732	.5197
23	.9099	1.4728	.5196
24	.9093	1.4724	.5195
25	.9086	1.4721	.5196
30	.9053	1.4701	.5193
35	.9021	1.4681	.5189

Castor Oil, 3.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9602	1.4799	.4998
19	.9595	1.4795	.4997
20	.9589	1.4791	.4996
21	.9582	1.4788	.4997
22	.9575	1.4784	.4996
23	.9569	1.4780	.4995
24	.9562	1.4777	.4996
25	.9555	1.4773	.4995
30	.9522	1.4755	.4994
35	.9488	1.4738	.4994

Lard Oil, 13.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9137	1.4694	.5137
19	.9130	1.4690	.5137
20	.9122	1.4686	.5137
21	.9116	1.4682	.5136
22	.9109	1.4678	.5136
23	.9102	1.4674	.5135
24	.9095	1.4670	.5135
25	.9088	1.4666	.5134
30	.9053	1.4647	.5133
35	.9019	1.4627	.5130

Peanut Oil, 19.

T.	D.	N.	$\frac{N-1}{D}$.
18	.9187	1.4725	.5143
19	.9180	1.4721	.5143
20	.9173	1.4717	.5142
21	.9164	1.4713	.5143
22	.9157	1.4709	.5143
23	.9151	1.4705	.5142
24	.9144	1.4701	.5141
25	.9138	1.4696	.5139
30	.9103	1.4678	.5139
35	.9069	1.4658	.5136

The numbers in the column headed $\frac{N-1}{D}$ are not quite constant, but do not vary more than is the case with many organic substances. In most cases the refractive index seems to decrease somewhat more rapidly than does the specific gravity.

The saponification equivalents found for several of these oils, sesamé, olive, and cottonseed, show a mean molecular weight of about 870. From this the *molecular* refractive energy, $M\left(\frac{N-1}{D}\right)$, is about 448, which coincides very well with the atomic refractive energies, $C = 4.85$, $H = 1.50$, and $O = 3$.

If an oil in the above table contained only tri-olein these numbers would lead to 450.4. A mixture of tri-olein and tri-stearin would yield nearly the same result; while tri-palmitin, having a lower

molecular weight, would make the number slightly smaller. A mixture of 8 parts of tri-olein and 2 parts of tri-palmitin would give 447.2, and this is approximately the composition of the above oils.

In the olive oils the specific gravity at 20° C. varies between .9126 and .9136. These values are about the same as commonly given for the finest cold pressed oils and are within the limits of the United States and British Pharmacopœias. Schaedler gives .9143 as the specific gravity of a pure sample at 20°, but states that in hot pressed oils rich in palmitin it may be as high as .922 at the same temperature. The refractive indices at 20° vary from 1.4695 to 1.4711, and the specific refractive energy from .5143 to .5162 at the same temperature.

In the six samples of cottonseed oil examined the variations in the specific gravity at 20° are between .9186 and .9210. These numbers are all greater than those with olive oil. The refractive indices vary from 1.4722 to 1.4741, and the refractive energies between .5127 and .5161 at 20°. These last numbers are nearly the same as with olive oil.

It will be noticed that the values given for the specific gravity are much lower than those usually quoted. Allen places the density of the crude oil between .928 and .930, with that of the refined between .922 and .926. Dietrich (Dingler's Poly. Jour. 1885, 127) places the density of the pure oil at 23° between .917 and .921. These numbers have evidently been obtained from samples richer in palmitin than were those examined by me.

In the three samples of sesamé oil the specific gravity at 20° varies between .9181 and .9199, the refractive indices between 1.4735 and 1.4748, and the quotient $\frac{N-1}{D}$ between .5150 and .5161. These numbers are similar to those for cottonseed oil.

In mustard oil the density is lower; at 20° the three samples vary between .9116 and .9127, their refractive indices between .14740 and 1.4746, and the refractive energies between .5198 and .5201. These figures are higher than found for other oils and may have a practical value. In castor oil we have a high gravity and low refractive energy.

The specific gravities found for lard oil and peanut oil do not differ materially from those usually given, and there seems to be nothing unusual about the refraction.

In many cases determinations of refractive index have a practical use in the identification of organic liquids and also in quantitative valuation.

Alex. Müller has recently proposed the use of the Abbé refractometer in the examination of butter, and Skalweit (Rept. anal. Chem. 1886, pp. 181 and 235) has carried out a number of tests to show the value of the method. It appears from his tests that *butter oleine* (separated after melting by partial cooling and pressure) has a lower refractive index than any oil in the above table, and also lower than that of the various solid products as butterine and oleomargarine.

Skalweit's observations have undoubtedly a practical value, but his method necessitates the use of the Abbé refractometer. I have found that results almost as sharp can be obtained by using solutions of the fats made with definite mixtures of alcohol and chloroform, and determining the minimum deviation in the usual manner with the Meyerstein or similar instrument. The above experiments show that a determination of the refractive power coupled with that of the specific gravity may prove of value in the identification of other fatty oils.

CHICAGO, *December*, 1887.

ON THE TREATMENT OF NATURAL SILICATES WITH HYDROCHLORIC ACID AS A MEANS OF ASCERTAINING THEIR STRUCTURE.

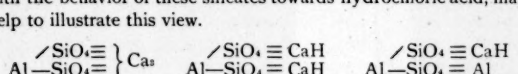
BY E. A. SCHNEIDER.

In the March number of this journal, Professor F. W. Clarke has published some very interesting remarks on the chemical structure of natural silicates. In speaking of the real difficulties which are met with in this kind of researches, Professor Clarke observes very justly that though it is not possible to ascertain the true molecular weight of silicates on account of their being non-volatile solids, their chemical structure can be determined by the study, for instance, of the alterations they undergo in nature. Now, it is a well known fact that alterations through weathering are

chiefly due to the carbonic acid of the air. The action of carbonic acid on minerals has been undoubtedly tried in chemical laboratories, but no decisive results are recorded. This may be partially due to the fact that this process is too slow for the patience of the average chemist. In this respect hydrochloric acid is preferable. It acts more quickly and with more energy on the natural silicates than carbonic acid; some silicates are completely decomposed by it, some partially, and some not attacked at all. This varying behavior of the silicates towards hydrochloric acid has been made use of by the authors of mineralogical tables for the purposes of classification, but to derive from these facts new material for the explanation of the structure of the natural silicates has apparently not been thought of. And still it seems to be promising.

Supposing a number of silicates which contain the same constituents, but in varying proportions, whose relationship has been made probable by many indications, and which are partially decomposed by hydrochloric acid, should be treated under exactly the same conditions with hydrochloric acid, and it should be found that various but gradually increasing or decreasing amounts of the same constituents have been extracted, should we not to some extent be entitled to arrange the members of such a series of silicates accordingly and draw some conclusions as to their structure?

The contemplation of the structural formulas which Professor Clarke gives for grossularite, prehnite and anorthite, in conjunction with the behavior of these silicates towards hydrochloric acid, may help to illustrate this view.



We observe in this series of formulas a remarkable gradation; and we observe the same gradation in the behavior of these silicates towards hydrochloric acid: grossuralite is insoluble in hydrochloric acid, prehnite is decomposed by this acid without gelatinising, and a certain variety of anorthite (from Mount Somma, according to Dana) with separation of gelatinous silica.

The fact that grossularite gelatinises with hydrochloric acid after ignition is also of some interest. It is possible that ignition modifies the structure of the grossularite in a way which approaches it very near to prehnite and anorthite.

The hypothesis of Sterry Hunt and of Tschermak, that the triclinic feldspars consist of various mixtures between albite and anorthite as two extremes, appears to be confirmed also by the behavior of the triclinic feldspars towards hydrochloric acid. Anorthite is soluble and albite insoluble in hydrochloric acid. Oligoclase, which is mainly a soda feldspar with a small percentage of lime, is "not materially acted upon by acids" (Dana); andesite, which contains more lime, is said to be "imperfectly soluble in acids" (Dana); and labradorite, which is the richest in lime of all the triclinic feldspars, is, according to B. v. Cotta,[1] "unlike other feldspars, thoroughly soluble in heated muriatic acid." According to Dana, it "is decomposed with difficulty by muriatic acid, generally leaving a portion of undecomposed mineral."

Do the hydrochloric acid extracts contain mainly lime salts, or sodium and lime salts proportionately to the lime and soda in the feldspars? These questions are certainly worthy of consideration, and if answered, would throw some additional light on the theory of Sterry Hunt and Tschermak.

Next to the triclinic feldspars, the minerals of the amphibole group show a peculiar behavior towards hydrochloric acid. B. v. Cotta[2] makes the statement that the "varieties of amphibole richest in iron are partially decomposed by muriatic acid; other varieties are little affected by that acid." If we class wollastonite, $CaSiO_3$, in this group, we have, however, a notable exception. This silicate gelatinises readily with hydrochloric acid. This fact is peculiarly interesting, as another metasilicate which belongs to this group, enstatite, $MgSiO_3$, is perfectly insoluble in hydrochloric acid. Moreover, wollastonite and enstatite show differences in their crystallographic character; the first is monoclinic, the second orthorhombic.

As the magnesia-lime silicates of the amphibole group can be considered, at least chemically, as wollastonite or as enstatite in which a part of the lime has been substituted by magnesia and *vice versa*, and some of these minerals are partially decomposed by hydrochloric acid, a similar line of research as in the case of the triclinic feldspars is indicated.

It is known of some minerals of the amphibole group (as well as of those of the garnet group) which contain ferrous oxide, that their decomposition by muriatic acid is very superficial, and

[1] "Rocks Classified and Described." B. v. Cotta. [2] Ibid.

that they yield to the acid nothing but iron. This interesting peculiarity has not been further studied, although the amphibole group contains material enough for such an investigation if we take into consideration the great range of variations in the percentages of ferrous oxide among the minerals of this group. The fact that in many instances the ferrous oxide is found together with one only of the oxides of calcium or magnesium should facilitate a comparative investigation.

I give here, to illustrate this view, a number of analyses from J. D. Dana's "System of Mineralogy."

	Anthophyllite, magnesia-iron amphibole.[1]	Hypersthene.[2]	Hedenbergite, iron-lime pyroxene.[3]	Cummingtonite, iron-magnesia amphibole.[4]	Hypersthene.[5]	Grisnerite, iron amphibole.[6]
SiO_2	55.20	52.88	47.78	51.09	51.35	43.9
Al_2O_3	...	3.90	...	.95	...	1.9
FeO	11.82	18.23	27.01	32.07	33.92	52.2
MnO	...	...	...	1.50	...	...
MgO	30.37	22.22	...	10.29	11.09	...
CaO	...	3.55	22.95	tr.	1.84	.5
H_2O	2.25	.56	...	3.04	.50	...
Na_2O	...	...	...	.75	...	...

Some preliminary experiments have convinced me that the most trustworthy and uniform results will be obtained by digesting the finely triturated mineral powders with hydrochloric acid (which boils unchanged at 110° under the normal pressure) in sealed tubes[7] of hard glass. The most suitable (because the easiest to regulate) temperature for the digestions is that of boiling water at 760 mm. pressure. As I have at present no laboratory accommodations at my disposal, I should be happy to see if any of my fellow-workers deem it worth while to carry out experimentally some of my suggestions.

[1] From Staten Island, analysed by Beck. [2] From Harzburg, analysed by Streng.
[3] From Arendal, analysed by Wolff. [4] From Cummington, analysed by Smith and Brush.
[5] From Skye, analysed by Muir. [6] From Collobrieres, analysed by Grisner.
[7] If the mineral powders are digested with the acid in open vessels, an unavoidable loss by evaporation takes place. As for the purposes of a comparative research it is important that all the experiments should be performed under strictly the same conditions, it would be necessary to replace the evaporated acid. I have found that by working in this manner, the greatest possible accuracy cannot be obtained, and propose therefore to use sealed tubes or other closed vessels.